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DEVELOPMENT OF CORROSION RESISTANT SURFACE TREATMENTS FOR ALUMINUM ALLOYS FOR SPOT-WELD BONDING

NORTHROP CORPORATION
AIRCRAFT DIVISION

MARCH 1975

FINAL REPORT
NOR 75-51

AIR FORCE MATERIALS LABORATORY
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

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This technical report has been reviewed and is approved for publication.

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The objective of this program was to develop a corrosion resistant spot-weld bonding system for aluminum aircraft primary structures. Anodizing and chemical surface treatment were investigated. Chemical and microscopic techniques indicated that the most suitable corrosion resistant surface on aluminum should be a boehmite surface, $\alpha Al_2O_3 \cdot H_2O$. Many anodizing and chemical treatment systems were able to produce this surface oxide; however, most of these systems produced surfaces that either showed poor corrosion

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Block 20. Abstract (Cont.)

resistance or could not be spot-welded. A treatment consisting of the standard FPL etch followed by 90-minute sealing in boiling sodium dichromate solution gave a weldable surface with good corrosion resistance. Adhesives were investigated for use in the spot-welding process. The best adhesive found was B.F. Goodrich A-1396B. This adhesive was modified by incorporating $ZnCrO_4$ and $SrCrO_4$ to make it more corrosion resistant. The addition of 3% by weight $SrCrO_4$ was found to give an adhesive that could be welded through and had improved corrosion resistance over the unmodified adhesive. The modified adhesive had too much flow during cure. This was corrected by use of 7% by weight Cab-O-Sil in the adhesive formulation. Spot welding parameters giving Class A welds have been developed for each alloy, each surface treatment (spot-weld etch, FPL etch, and FPL etch plus 90-minute dichromate seal) and each adhesive (A-1396B and chromate modified A-1396B). The selected spot-weld bonding system is FPL etch with 90-minute dichromate seal and the modified A-1396B adhesive. It has been evaluated under both stressed and unstressed environmental conditions. Results indicate that this spot-weld bonding system has the strength and corrosion resistance of the best corrosion resistant adhesive systems currently available.

PREFACE

This report was prepared by the Northrop Corporation, Aircraft Division, Hawthorne, California, under USAF Contract F33615-74-C-5027. The contract work was performed under Project No. 7340, Task No. 734002, and administered under the direction of the Air Force Materials Laboratory. The program monitor was Mr. T. J. Aponyi (MBC) of the Composites and Fibrous Materials Branch of the Nonmetallic Materials Division, AFML.

Mr. B. B. Bowen served as the Principal Investigator on this program. Other Northrop personnel who made major contributions in this research program were R. E. Herfert, K. C. Wu, H. R. Miller, and K. Wu.

The contractor's report number is NOR 75-51. This report covers work from 1 February 1974 through 1 February 1975.

This report was submitted by the authors 1 March 1975.

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INTRODUCTION

The application of spot-weld bonding as a joining method for aircraft structures has been hampered by the development of an aluminum adherend surface treatment which is both bondable and weldable. Previously successful spot-welding treatments do not yield an environmentally durable bond. Standard bonding treatments give surfaces which are difficult to weld.

This program was structured to solve the paradox by first characterizing the surface chemistry of the aluminum adherend in terms of the oxide layers produced by the various treatments that produce the most stable oxide layer. This oxide layer would then be controlled in thickness in a manner to obtain maximum durability consistent with a production spot-welding capability. Secondly, concurrent studies were to be conducted in the area of improving the corrosion resistance of the adhesive system used. Finally, these two approaches would be combined to evaluate and compare the strength and durability of spot-weld bonds made with and without an improved surface treatment and a corrosion inhibiting adhesive.

The study to establish the surface character and reproducibility is the Phase I segment of the program. Work on increasing the relative durability of the spot-weld bond by incorporating corrosion inhibitors within the adhesive layer is the Phase II segment of the program.

In Phase III, these two approaches are evaluated separately, combining the optimum developments of each and evaluating these against the baseline surface treatments, spot-weld etch, and metal-bond etch, using both the baseline and modified adhesives. This characterization defines both the improvements gained as well as the deficiencies remaining.

SECTION II

SUMMARY

The following paragraphs contain a summary of the significant accomplishments generated during the course of the contract effort.

1. The Phase I effort of the program has defined the requirements of an aluminum alloy surface which satisfies the requirements of Class A weldability and significantly improved bondline durability. These requirements are:
   a. An oxide layer of boehmite ($\alpha Al_2O_3 \cdot H_2O$)
   b. A carefully controlled thickness of a maximum of ~700 Å and a minimum of ~400 Å.
   c. The oxide layer must be produced in an acid solution such as the FPL etch, sulfuric acid anodize, chromic acid anodize, or phosphoric acid anodize to provide a tenacious, somewhat porous layer which forms a strong sealed bond with the metal adherend.
2. Surface treatment procedures which produce the above coating are:
   a. The FPL etch (sulfuric acid/sodium dichromate)
   b. The FPL etch plus a boiling water/sodium dichromate seal.
   c. A low voltage (1 VDC) sulfuric acid anodize plus a dichromate seal.
3. Based on the following considerations, the FPL etch followed by a 90 minute seal in boiling water/sodium dichromate solution was selected for characterization of bond strengths in Phase III.
   a. The FPL etch produces a thin coating of boehmite (100-400Å) which is not sufficiently stable to room temperature aging (degradation is noted in between 25-50 hours) to provide satisfactory out-time of the surface for manufacturing considerations.
   b. The low voltage sulfuric acid anodize process is very difficult to control in that the applied voltage is very low (~1 VDC) and the anodizing times are very short (in the order of 30-60 seconds) to produce the required oxide thickness.

c. The FPL etch plus 90 minute seal produces the required coating thickness and the surface has been determined to be stable to 300 hours of ambient exposure at 72F and 50% R.H.

4. The Phase II work defined the effectivity of adding small amounts of corrosion inhibiting modifiers to the baseline adhesive. This work resulted in a formulation consisting of B.F. Goodrich A-1396B containing 7% by weight Cab-O-Sil to prevent adhesive runoff during cure and 3% by weight strontium chromate to provide corrosion inhibition. This formulation is available from B.F. Goodrich designated as 0500-PE-130.

5. Concurrent with the surface treatment and adhesive developments, a complete set of welding parameters have been developed for deoxidized, FPL etched, and sealed FPL etched surfaces using both the baseline A-1396B adhesive and the chromate modified A-1396B. The welding theory used to develop these parameters is included in this report.

6. The Phase III characterization studies have shown:

   a. The importance of the boehmite oxide layer in promoting initial adhesive strengths and resistance to stressed environmental exposure.

   b. The effectivity of modifying the adhesive with small amounts of very slightly soluble chromates in improving bondline durability.

   c. A spot-weld bonded system consisting of surface treatment, welding capabilities, and adhesive formulation which exhibits strengths and durability nearly comparable to the presently available structural adhesives. Strength levels of 4000-6000 psi in spot-weld bonded and adhesive bonded lap shear are attainable with A-1396B and PE-130 adhesive. Durability resistance to stressed environment has been compared to FM-123/BR-127 on Northrop IRAD. Results to date indicate comparable durability.

SECTION III

TECHNICAL DISCUSSION

PHASE I - SURFACE TREATMENT DEVELOPMENT

The original goal for this phase of the program was to develop a surface on the aluminum alloys which: (a) had a contact resistance of ≅1000 μohms ± 10% with a stability of 40 hours without change at R.T., (b) consisted of greater than 90% of the surface oxide as the $\alpha Al_2O_3 \cdot H_2O$ composition and crystal structure, and (c) contained sufficient corrosion inhibiting ions or compounds to provide in situ reformation of the oxide if moisture permeation occurred.

Known procedures for developing the alpha oxide form on the aluminum surface in varying thicknesses are FPL etch, boiling water immersion, and electrolytic anodizing. Two procedures for incorporation of oxidizing ions or compounds into the crystal structure are the addition of such compounds within the boiling water immersion and the electrolytic anodize baths.

The first of the above procedures tried for producing the required oxide surface was the sulfuric acid anodize process. Standard bath concentrations and procedural steps are shown in the Appendix.

Validation of the process was conducted by anodizing standard 3- by 5-inch aluminum panels and submitting these to standard salt spray exposure. Following qualification, a series of panels were treated similarly except at reduced times under anodizing conditions. Following treatment, including dichromate sealing, surface resistances were measured. Values obtained are shown in Table I for a standard 10 VDC anodizing in sulfuric acid.

TABLE I

SURFACE RESISTANCE VERSUS ANODIZING TIME AT 10 VOLTS IN SULFURIC ACID

ALLOY	ANODIZING TIME	CONTACT RESISTANCE
2024-T3 Bare	5 min.	Infinite
2024-T3 Clad	5 min.	Infinite
2024-T3 Bare	2 min.	2000-5500 μOhms
2024-T3 Clad	2 min.	1800-4500 μOhms
7075-T6 Bare	2 min.	2100-4000 μOhms
7075-T6 Clad	2 min.	3000-4500 μOhms
7075-T6 Bare	2 min.	1000-2100 μOhms
7075-T6 Bare	1½ min.	3200-6300 μOhms
7075-T6 Bare	1 min.	1200-4300 μOhms
7075-T6 Bare	½ min.	2000-5400 μOhms

Based on the high contact resistances shown in Table I even for the very short sulfuric acid anodizing times, chromic acid anodizing was evaluated as an alternate method. A standard chromic anodize bath (see Appendix) was set up and evaluated as before by preparing samples for electron diffraction analysis and salt spray exposure tests. When standard baseline conditions were established, various reduced anodizing times were tried in the attempt to reduce the thickness of the coating. The results of all attempts showed an infinite surface resistance making the chromic acid anodize even less desirable than the sulfuric. This is attributed to the higher anodizing voltages required (40-50 volts versus 10-17 volts) and the required stepwise (5 volt increment) increase to the anodizing levels. It is felt that oxide surfaces are formed very quickly and then build up to a corrosion resistant thickness over a period of time.

Additional testing has been conducted with the sulfuric anodize bath using a lower voltage and current density. Specimens were prepared using a 5 volt anodizing voltage for times of 30 seconds and two minutes. Contact resistances for both times were approximately 1000 to 2000 μohms. More importantly, the oxide resulting from treatment was $\alpha Al_2O_3 \cdot H_2O$. Being able to obtain the required oxide layer at lower voltages allowed further experimentation at voltages of one and three volts and changes in electrolyte concentrations.

A slower method of producing the oxide layer involved chemical treatment of the surface in oxidizing baths. Primary among the chemical treatments are the two procedures known to provide a nearly pure $\alpha Al_2O_3 \cdot H_2O$ (boehmite) surface on all the aluminum alloys, i.e., FPL etch and boiling water seal containing sodium dichromate. The FPL etch forms a very thin coating of boehmite with a fairly low contact resistance. This contact resistance varies from 30 to 200 μ ohms depending on batch variation and alloy surface. Specimens were prepared through the FPL etch and immersed in the boiling water/sodium dichromate seal solution. Resistances on 7075-T6 bare aluminum averaged about 250 μohms after a 30-minute seal up to about 800 μohms after a 4-hour seal. However, the variation after 4 hours was from 325 to 2400 μohms.

The Alodine 1200 process has also been investigated as a chemical means of producing the oxide layer. Surface resistance measurements on 7075-T6 bare aluminum treated by this procedure were high, in the range of 1800 to 6000 μohms, and it was subsequently determined that the oxide layer was a more hydrated form of boehmite with a lesser degree of crystallinity. Evaluation of this process is being discontinued.

A literature survey was conducted in conjunction with the experimental phase of the surface treatment investigations to confirm and explain the experimental evidence gathered. The most significant review article covered in this survey is "Oxides and Hydroxides of Aluminum," Technical Paper No. 19 by Karl Wefers and Gordon M. Bell, published by Alcoa Research Laboratories in 1972. This paper provides a comprehensive review of all the various aluminum oxides or hydroxides with the procedures for characterization and synthesis, the standard nomenclature, and numerous physical and chemical properties of each.

The first pertinent factor covered in the paper is that there are four common and naturally occurring forms of the aluminum oxide that affect the direction of this program. In terms of standard nomenclature, these are:

Bayerite - $\beta Al_2O_3 \cdot 3H_2O$
Boehmite - $\alpha Al_2O_3 \cdot H_2O$
Diaspore - $\beta Al_2O_3 \cdot H_2O$
Corundum - αAl_2O_3

A phase diagram showing the occurrence of these forms at various temperatures and pressures in the presence of water or water vapor is shown in Figure 1 As shown in this phase diagram, only two forms of the oxide are of direct interest to this program, namely, bayerite and boehmite. Bayerite forms naturally on the surface of the aluminum adherend at ambient conditions of temperature and pressure to a temperature of 100C. Boehmite forms above 100C or will form due to electrolytic anodization. These oxide formations have been confirmed by electron diffraction analyses of various prepared surfaces as will be discussed in greater detail later in this report.

The second factor determined from the Alcoa paper is that the heat of formation of bayerite is approximately -612.6 kcal/mole and that of boehmite is -463.4 kcal/mole indicating the formation of bayerite as the stable end product. This indicates a fairly large activation energy restricting the conversion of boehmite to bayerite at room temperature.

Surface treatment development then concentrated on producing a controlled thickness boehmite coating on the various aluminum alloys by anodization. Procedures for thin film coatings were worked out using low voltage sulfuric acid and phosphoric acid anodizing. Initially, a set of 0.064" x 1" x 2" samples were prepared by either degreasing, alkaline cleaning, and FPL etch deoxidize or degreasing, alkaline cleaning and Amchem 7/Nitric acid deoxidize prior to anodizing. These samples were then anodized for 30 seconds at either 1.0 VDC or 3.0 VDC and then dichromate sealed in accordance with standard procedures (see Appendix). Surface contact resistances measured on three pairs each of these samples are as follows:

	FPL ETCH DEOXIDIZE	AMCHEM 7/NITRIC ACID DEOXIDIZE
Anodize 1 VDC for 30 seconds	1. 75, 85, 33 μohms 2. 58, 73, 77 μohms 3. 98, 42, 75 μohms	1. 225, 360, 190 μohms 2. 60, 220, 200 μohms 3. 45, 70, 50 μohms
Anodize 3 VDC for 30 seconds	1. 45, 40, 38 μohms 2. 37, 77, 130 μohms 3. 52, 65, 73 μohms	1. 390, 345, 370 μohms 2. 510, 340, 110 μohms 3. 350, 290, 190 μohms

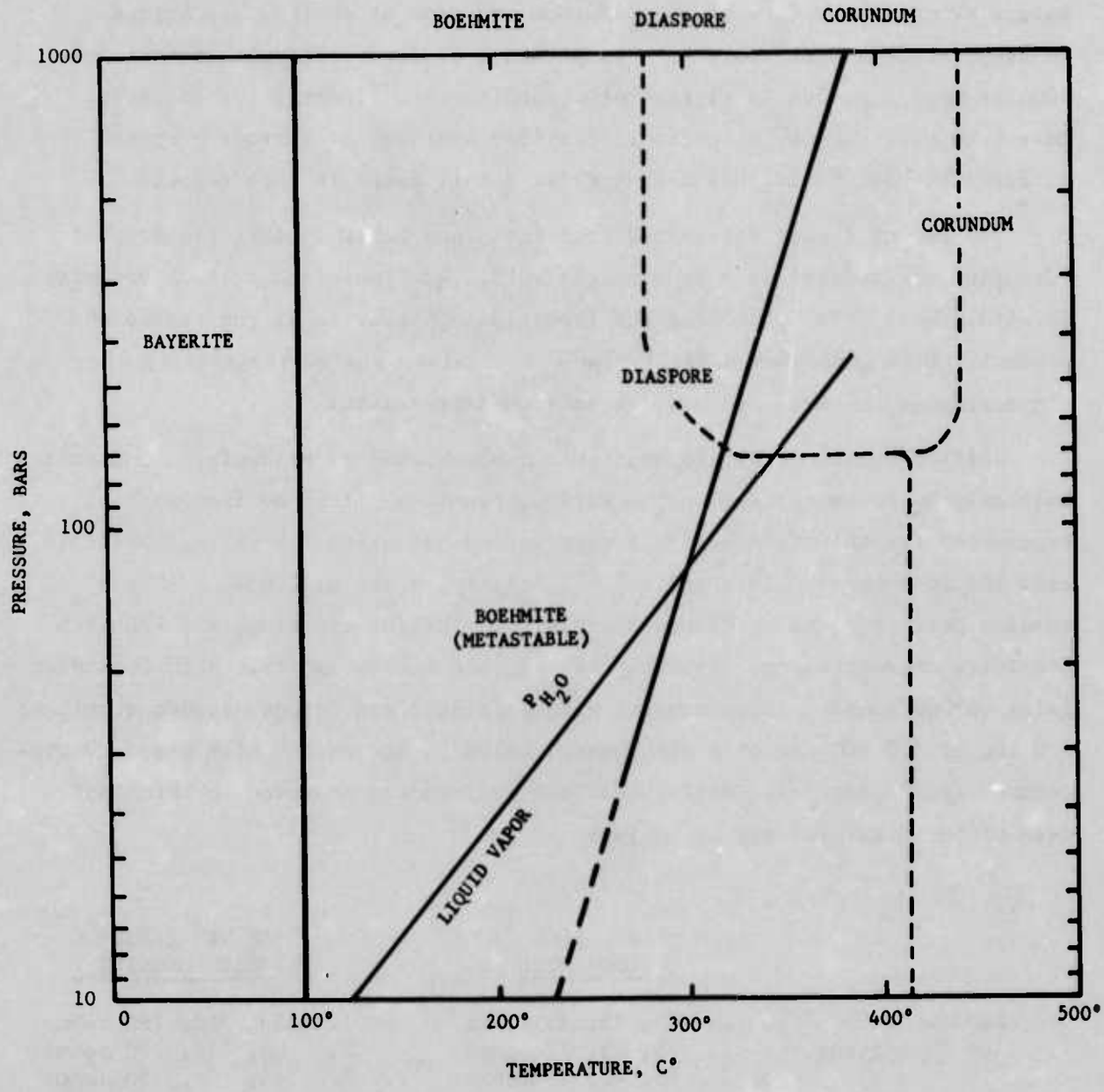

FIGURE 1. THE SYSTEM $Al_2O_3 \cdot H_2O$

REPRODUCED FROM: "OXIDES AND HYDROXIDES OF ALUMINUM," TECHNICAL PAPER NO. 19, ALCOA RESEARCH LABORATORIES, 1972, KARL WEFERS AND GORDON M. BELL

These results were very encouraging since they were the first to fall within the range desired by the original program goals. Accordingly, additional samples were prepared selecting the Amchem 7/Nitric acid deoxidize treatment and 1.0 VDC and 2.0 VDC anodizing voltages to determine the time versus surface resistance characteristics. The average results of these tests are depicted in Figure 2.

In working out the parameters on phosphoric acid anodizing, it was found that the following conditions gave a very thin oxide coating with a surface contact resistance in the nominal range of 100 to 500 μohms on the four alloy configurations.

Procedural Steps

1. Vapor degrease.
2. Alkaline clean - Turco 4215.
3. Deoxidize - Nitric acid/Amchem 7.
4. Anodize - 20-25 min. @ 10 $\pm$1 VDC in 11-16 oz./gal. phosphoric acid @ R.T.
5. Oven dry at 150F-160F.

Note: Rinse in deionized water after steps 2, 3, and 4.

In low-voltage sulfuric acid anodize, voltages of 1.0, 1.5, and 2.0 VDC were used for times of 2 through 10 minutes. It was found that sulfuric acid anodizing at 1.5 volts for 10 minutes gave a fairly uniform coating with a contact resistance of 300 to 700 μohms.

A series of 1" x 2" x 0.064" samples were prepared by the two above anodizing procedures (1.5V sulfuric and 10V phosphoric acid) and submitted for development of welding parameters. At this point in the program, it was found that these surfaces were not weldable to produce Class A welds and that contact resistance, per se, was not a valid measure of the weldability of a surface consisting of a boehmite layer. A more complete discussion of welding problems encountered may be found in the section on "Welding Parameters Development."

Since it was determined that neither sulfuric nor phosphoric acid anodized surfaces were weldable and further that the required degree of control of coating thickness was not possible with the acid anodize treatments, it was therefore decided to attempt the development of a process utilizing a "barrier layer"

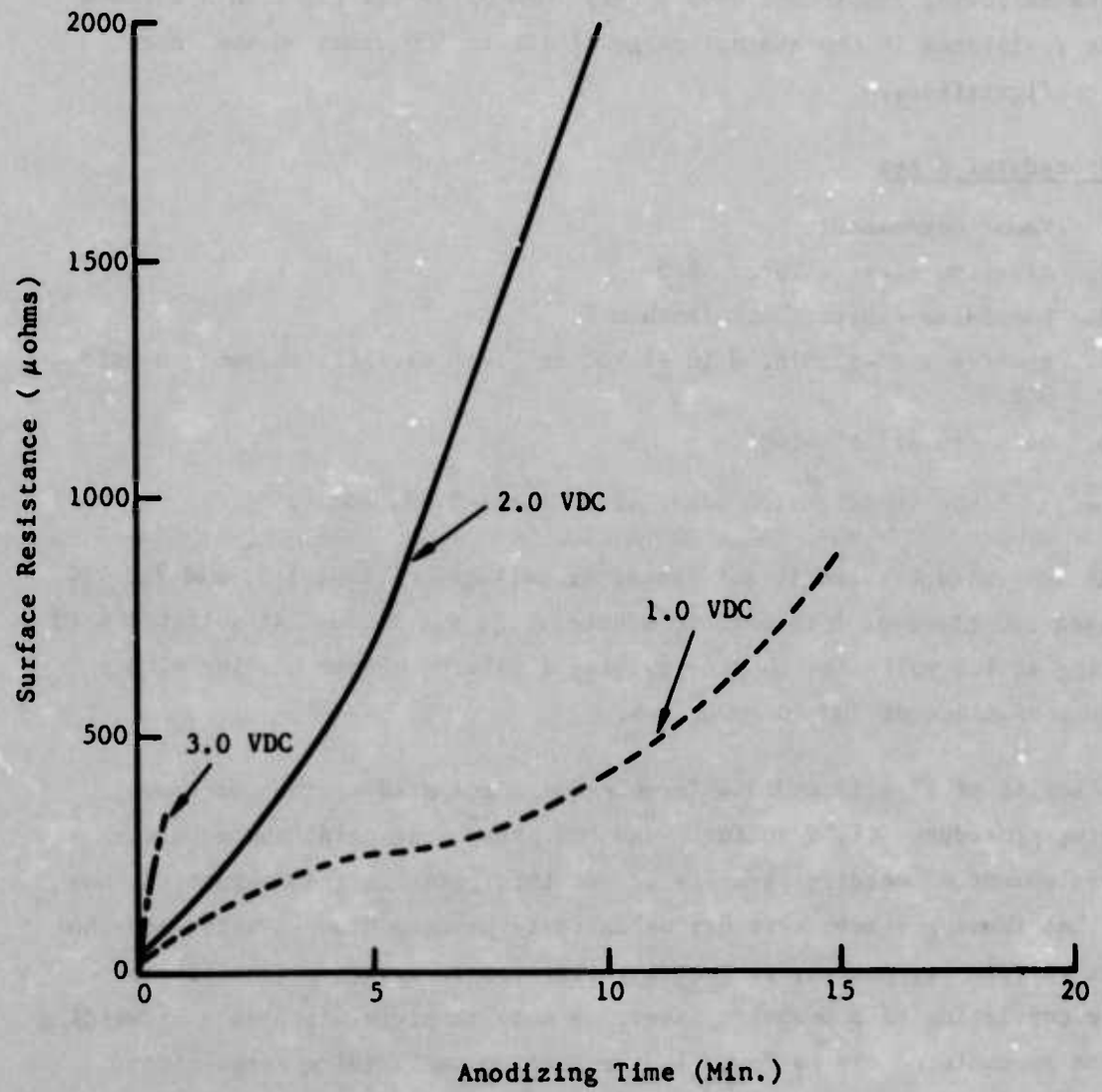

FIGURE 2. ANODIZING CHARACTERISTICS - CONTACT RESISTANCE VS. TIME

anodizing solution. These solutions are non-reactive to the aluminum surface as contrasted to the acid baths which will dissolve the surface as the coating is built up. This fact makes the process controllable by only controlling the applied voltage, in which case an oxide layer of a theoretical thickness of 12Å to 14Å per volt applied is all that is built up.

The solution selected for development on this program is a 3 percent ammonium tartrate solution operated at room temperature at a pH of 5.5. Preparation prior to anodizing is the same as the Northrop standard spot-weld cleaning procedure and consists of vapor-degrease, alkaline clean and nitric acid/Amchem 7 deoxidize. Anodizing voltages of 10, 20, 30, and 40 volts D.C. were tried for the first screening phase of the investigation. Surface contact resistances of all these coatings were in the range of 150 to 500 μohms. However, none of the surfaces were weldable. The second trial set of voltages were 1, 2, 3, 4, and 5 volts D.C. Of these voltages, 1 through 4 volts gave fairly easily welding surfaces and the 5 volt anodize was somewhat borderline in that expulsion occurred sporadically. Welding parameters were used to select the final operating voltages for the anodize treatment.

An alternate technique of producing thin layer oxide coatings on the surface was developed by using the standard hot water/dichromate sealing process. Surface pre-treatments of either deoxidizing or FPL etching were used and then followed by 30, 60, and 90 minute dichromate sealing. It was found that surfaces prepared by FPL etch followed by a 90-minute dichromate seal had the maximum oxide layer thickness that could be spot-welded successfully. Both surface treatments, ammonium tartrate anodize and FPL etch/dichromate seal, were carried forward in the program until an optimum choice could be made either by initial strengths or durability of the adhesive bond.

MICROSTRUCTURAL CHARACTERIZATION

Introduction and Summary

Throughout the program, microstructural analysis has been used to physically, chemically, and crystallographically characterize the anodic films developed on aluminum base alloys through various techniques. In addition, failure mechanics associated with weldbonded specimens and simple adhesive/metal bonded specimens have been studied. The stability of oxides exposed to "shelf-life" environment were evaluated for the more promising systems.

Characterization of the surfaces developed on aluminum base alloys (2024-T3 and 7075-T6) through the use of both chemical and anodic processes were monitored using the following techniques:

1. Auger Electron Spectroscopy (AES) monitored the surface chemistry and profiled chemical changes through the oxide layer.
2. Scanning Electron Microscopy (SEM) was used to physically characterize the oxide and measure relative thickness. In addition, the SEM was used to perform failure mechanism studies on selected systems.
3. Selected Area Electron Diffraction (SAD) in either the SEM or transmission electron microscope was used to characterize the crystalline form of the oxide formed by either chemical or anodic processes.

A technique was developed to provide an inexpensive method of examining the oxide character and thickness on the SEM. A wide variety of prepared surface treatments have been characterized as to type and thickness. These have included (1) FPL etched, (2) FPL etch plus dichromate seal, (3) ammonium tartrate (high and low voltage), and (4) sulfuric acid (high and low voltage).

Thickness of oxide layers as a function of chemical or anodic growth were measured, and crystallographic analysis was performed to verify the existence of the $\alpha Al_2O_3 \cdot H_2O$. Series of samples were run and evaluated to determine the reproducibility of the oxide growth process from sample to sample.

Failure analyses in terms of a proposed "durability" surface model were performed on adhesive/metal interfaces as well as weldbonded specimens in the as-bonded and stress-corrosion tested conditions.

Chemical Characterization

A series of specimens of 2024 bare and clad and 7075 bare and clad were prepared with the following surface treatments:

Chemical Processes

1. $HNO_3 + Na_2SO_4$ (Room Temperature)
2. $HNO_3 + Na_2SO_4$ (Elevated Temperature)
3. Lockheed (08) (See Appendix 1)
4. Northrop's Deoxidizer (Process Bulletin C-27)(See Appendix 1)
5. FPL Etch
6. FPL + Dichromate Seal

Anodic Processes

1. Phosphoric Acid Anodize
2. Low Voltage Sulphuric Acid Anodize
3. Ammonium Tartrate

Electron diffraction analyses were performed on the as-prepared surface to determine the crystalline character of any oxides present. The Hitachi HU11A transmission electron microscope was used for this. Auger spectrographic analysis was performed after exposure to 10^{-9} torr vacuum for 24 hours on each treated surface in the as-treated condition, 50Å below the surface, 500Å, 1000Å, 2000Å, etc., or until the oxide disappeared or depth of oxidation could be extrapolated. The presence of *a* oxide was found in the hot HNO_3 - Na_2SO_4, C-27 and FPL and FPL + dichromate seal chemical surface preparations. Only in the FPL type preparations was the oxide entirely *a*. The thickness of the oxide appears to increase where definite oxide forms are present.

Table II shows a summarization of the microstructural analyses performed on the chemical and anodic processes.

A representative profile/chemistry plot is shown for the FPL (metal bond) and spot weld etchant as shown in Figure 3.

Physical Characterization

The changes in morphology of the surface layer of aluminum adherends following different chemical pretreatments were studied by scanning electron microscopy (SEM) directly and by transmission electron microscopy (TEM) using reflection high energy electron diffraction (RHEED) techniques. RHEED studies were carried out on a Hitachi HU11A electron microscope with the standard high resolution electron diffraction holder mounted above the final projection lens pole piece. Transmission selected area electron diffraction analyses were not performed because this would entail a stripping of the surface layers. It was felt that such a stripping could result in a morphological change and, thus, an analysis of the layer in situ would be more reliable. Where an analysis of a potentially stratified layer is required, ion milling is being used to profile various levels of the oxide layer. Selected thicknesses are removed and then RHEED characterization is performed.

Physical examination of the prepared surfaces is performed using the scanning electron microscope. Specimens are vacuum coated with 100Å of gold to minimize charging effects. A new technique has been developed for the analysis of the extremely thin oxide layer coatings. In this technique, sections of the panel 1/4" X 1" are bent around a 1/4" mandrel to a bend angle of either 90° or 180°, depending on which angle is required to stress the oxide layer sufficiently to cause fracture. These sections are then mounted in the SEM such that they may be viewed at 90° to the fractured bent surface or at other selected angles such that the edge of the oxide layer may be viewed directly (See Figure 4). With this technique, various magnification ratios were evaluated to determine the proper ratio to best characterize the type of oxide layer (barrier, porous or sealed), to qualitatively assess the relative thickness of the layer, and to qualitatively assess the tenacity of the layer.

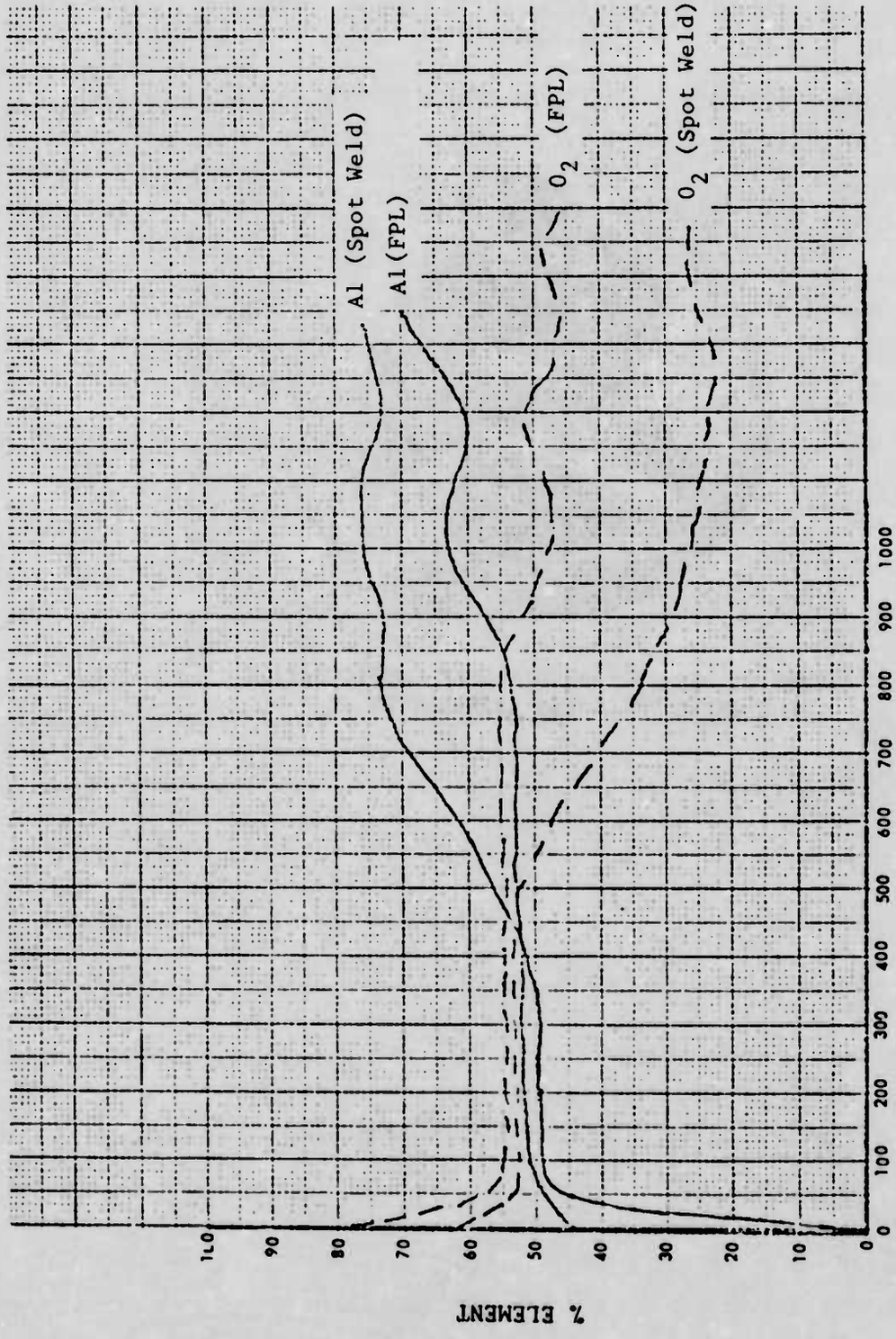

FIGURE 3. Al AND O_2 ANALYSES USING THE AUGER ELECTRON SPECTROGRAPH

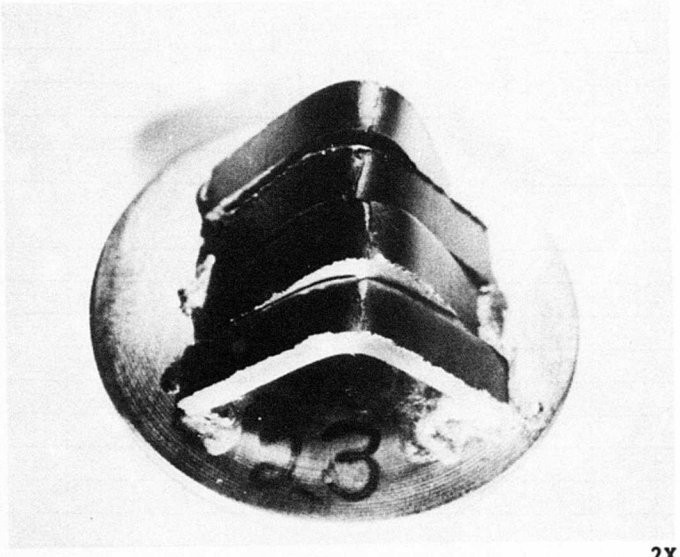

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FIGURE 4. SEM 90° BEND SAMPLE CONFIGURATION FOR OXIDE THICKNESS EXAMINATION

TABLE II

SUMMARIZATION OF OXIDE CHARACTER AFTER VARIOUS PROCESSES

ANODIC PROCESSES

PROCESS & MATERIAL	THICKNESS	TYPE	DESCRIPTION	
Phosphoric Acid Anodize				
2024-T3 Bare	~2400Å	Porous, Unsealed	$\alpha Al_2O_3 \cdot H_2O$	
7075-T6 Bare	"	" "	"	
2024-T3 Clad	~5200Å	" "	"	
7075-T6 Clad	"	" "	"	
Low-Voltage Sulfuric Acid Anodize				
2024-T3 Bare	~1900Å	Sealed, Porous	$\alpha Al_2O_3 \cdot H_2O$	
7075-T6 Bare	"	" "	"	
2024-T3 Clad	"	" "	"	
7075-T6 Clad	"	" "	"	
Ammonium Tartrate Anodize				
2024-T3 Bare	~1500Å	Barrier	$\alpha Al_2O_3 \cdot H_2O$	No change after 300 hrs. exposure to air.
7075-T6 Bare	"	"	"	
2024-T3 Clad	"	"	"	
7075-T6 Clad	"	"	"	

CHEMICAL PROCESSES

PROCESS & MATERIAL		THICKNESS	TYPE	DESCRIPTION	
HNO_3-Na_2SO_4 (RT)	2024-T3 Bare	<100Å	Barrier	Only Al, no oxides detected	Surface Al, S, C, O_2; 50Å Al, Trace O_2; 100Å Al
"	2024-T3 Clad	"	"	"	"
HNO_3-Na_2SO_4 (Hot)	2024-T3 Bare	~500Å	Barrier	Al & mixtures of $\alpha + \beta$ oxides (80% β 20% α)	Surface Al, C, N_2, S, Na, O_2 50Å Al, N_2, O_2; 100Å Al, O_2 500Å Al
HNO_3-Na_2SO_4 (RT)	7075-T6 Bare			Only Al, no Al_2O_3 structures detected	Surface Al, S, C, N_2, Na, O_2
"	7075-T6 Clad			"	"
HNO_3-Na_2SO_4 (Hot)	7075-T6 Bare		Barrier	Al & oxides of α, β, ~10% α presen	Surface S, C, N_2, O_2, Zn, Cu
HNO_3-Amchem 7	2024-T3 Bare	~1250Å	Barrier	Al & mixtures of $\alpha + \beta$ (70% β 30% α)	Surface Al, S, C, N_2, O_2 50Å Al, N_2, O_2 500Å Al, N_2, O_2 1000Å Al, O_2
HNO_3-Amchem 7	2024-T3 Clad	~750Å	Barrier	Al & mixture of $\beta + \gamma$, no α detected	Surface Al, C, N_2, O_2 50Å Al, N_2, O_2 500Å Al, N_2, O_2 1000Å Al
HNO_3-Amchem 7	7075-T6 Bare		Barrier	Al & mixture of $\alpha + \beta$, ~15% α	Surface S, C, N_2, O_2, Zn, Cu
HNO_3-Amchem 7	7075-T6 Clad		Barrier	Al & βAl_2O_3	Surface S, C, N_2, O_2, Fe
Lockheed Spot-weld Etch	2024-T3 Clad	~1250A	Barrier	Semi-crystalline oxide, probably β or γ	Surface Al, P, S, C, N_2, O_2 50Å Al, N_2, O_2; 500Å Al, O_2 1000Å Al, O_2; 1500Å Al
FPL on	7075-T6 Bare	~400Å	Barrier	$\alpha Al_2O_3 \cdot H_2O$	After 25 hrs. exposure to air, presence of bayerite $\beta Al_2O_3 \cdot H_2O$ detected, increasing in amount to approximately 50% after 150 hrs. exposure.
" "	" Clad	"	"	"	
" "	2024-T3 Bare	"	"	"	
" "	" Clad	"	"	"	
FPL + Dichromate Seal					
	7075-T6 Bare	~700Å	Sealed, Porous	$\alpha Al_2O_3 \cdot H_2O$	At 72 hrs., initiate X-ray line broadening. Continued increasing to 150 hrs. Stable from 150 to 300 hrs. (Suspected H_2O absorption)
	" Clad	"	" "	"	
	2024-T3 Bare	"	" "	"	
	" Clad	"	" "	"	

TABLE II

SUMMARIZATION OF OXIDE CHARACTER AFTER VARIOUS PROCESSES
(Continued)

In order to further clarify the meaning of various terms as applied to anodic or chemical oxides developed on aluminum the following list of definitions may be used.

Barrier Layer - first layer formed in anodic process and its thickness varies directly with forming voltage. It is thin, dense, and dielectrically compact.

Porous Layer - porous outer layer growing on the barrier layer during anodic process. Porosity depends on dissolution velocity and condition and rate of growth of film (related to operating conditions and type of electrolyte). Pore size and cell size related to operating conditions also.

Unsealed Porous - The porous oxide in the as-grown state. Pores are open and clean with direct paths from outer edge of porous oxide to barrier layer level.

Sealed Porous - the porous layer has been sealed with particular additives depending upon sealing process. This may vary from boiling water, chromates or silicates to metal salts which hydrolyze coating the pore capillaries with active compounds.

A specimen is obtained by removing the bend area of a 1/4" by 3/4" by 0.060" specimen bent to 90°. The bend area is then placed so that the electron beam will reflect from the surface of the bent area. In thicker layers, >500Å, only the layer diffracts the electron. In thinner specimens, a contribution is received from the aluminum substrate. Analysis of the diffraction pattern is performed by running standard patterns of Au to accurately obtain sample-to-photoplate distance for the respective pole piece and current conditions. The spotty patterns are analyzed using a circular film reader. Analysis is achieved by comparing with ASTM card file data for X-ray diffraction patterns. Table III shows a comparison of the "d-spacings" for the most commonly found oxides. In each oxide, 2 or 3 lines were "tagged" as indicators as to their presence or not in the oxide layer. These were:

Bayerite - 4.72, 4.36, 2.21
Boehmite - 6.11, 3.16, 1.86
Gamma - 2.41, 2.28, 1.98
Alpha - 3.48, 2.55, 1.74

In each oxide, distinct differences in d-spacings allowed positive identification of the oxide. In addition to the conventional RHEED techniques, the Kent-Cambridge S4-10 SEM has the capability for selected area diffraction techniques using the electron channeling effect. This method is considerably more rapid than conventional TEM procedures. It is more difficult to interpret. However, through the use of pre-prepared standards of the desired oxides, a quick visual comparison of patterns results in analysis.

The following oxide film layers have been analyzed for crystallographic morphology:

1. FPL Etchant
2. Phosphoric Acid Anodize
3. Sulfuric Acid Anodize
4. Chromic Acid Anodize
5. Ammonium Tartrate Anodize
6. FPL Etch plus Dichromate Seal
7. A.R. Aluminum Sheet
8. $HNO_3 \cdot Na_2SO_4$
9. HNO_3-AmChem 7
10. Lockheed Spot-Weld Etch

TABLE III

DIFFRACTION SPACINGS FOR SELECTED OXIDES OF ALUMINUM

BAYERITE		BOEHMITE		GAMMA		ALPHA	
d-SPACING	I/Io	d-SPACING	I/Io	d-SPACING	I/Io	d-SPACING	I/Io
		6.11	100				
4.72	100						
4.36	70						
						3.479	74
3.19	25						
		3.164	65				
3.08	1						
				2.7	2		
2.69	3						
						2.552	92
2.45	3						
				2.41	6		
						2.379	42
		2.346	53				
2.34	6						
2.28	3			2.28	6		
2.21	67						
				2.18	2		
						2.165	1
2.14	3			2.09	1		
						2.085	100
2.06	2						
		1.980	6				
				1.98	10		
1.97	3						
				1.95	6		
1.91	1						
		1.860	32				
		1.850	27				
1.83	1						
		1.770	6				
1.76	1						
						1.74	43
1.71	26						
1.68	2						
		1.662	13				
1.64	1						
						1.601	81
1.59	4						
						1.546	3

In each instance, 2024-T3 bare and clad and 7075-T6 bare and clad 0.060-inch nominal thickness sheet stock materials were evaluated. Surface of the as-received materials indicated primarily the presence of the Bayerite. The presence of Al was also noted due to the thin layer (approximately 100Å). This appears to be in contradiction with recently published results[1] where a "sub-oxide" of Al_2O_3 was reported to be a mixture of Al_2O and AlO on the as-received surface. Researchers[2] have reported that these two oxides exist in the gaseous state. Examination of the "pressure-temperature" phase diagram[3] would indicate that the Bayerite phase would exist in a normal room temperature aluminum surface. Crystallographic morphology did not appear to be affected by the nature of the substrate (bare or clad) or chemistry of substrate (Al-Cu or Al-Zn, 2024 and 7075, respectively). Of course, analysis was performed on the outer layer of the oxide. If there were any stratified layered effects, it would be surmised that the phases would have been detected since most oxides in the 100Å-400Å thickness would have been completely penetrated by the electron beam. This would certainly be true of the as-received, FPL, and ammonium tartrate "anodize" layers.

However, it must be postulated that a very thin layer of a different crystalline morphology may be present at the metal/adherend interface. This problem has been studied using ion milling to remove very thin layers of the adherend and successively examining it with RHEED techniques.

A tabulation of the "d-spacings" obtained from the RHEED patterns obtained from the 2024-T3 and 7075-T6 aluminum alloys are shown in Table IV. The actual patterns are not shown, since such data is rendered uninterpretable by graphic size changes.

TABLE IV

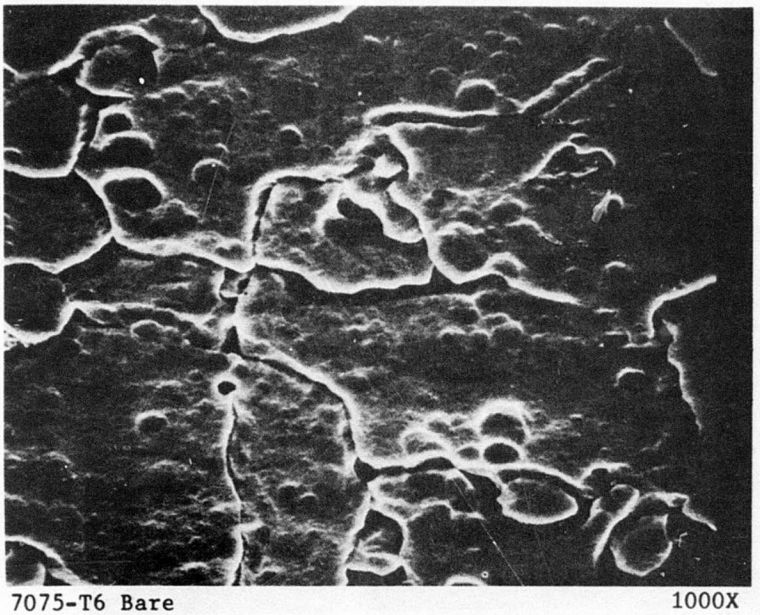
"d-SPACINGS" FROM RHEED PATTERNS OF VARIOUS OXIDE LAYERS

"FPL"		H_3PO_4		H_2SO_4		NH_4 Tartrate		FPL, Dichro. Seal		A.R. Al Sht.	
d,Å	I/Io	d,Å	I/Io	d,Å	I/Io	d,Å	I/Io	d,Å	I/Io	d,Å	I/Io
6.20	30	6.10	40								
				6.00	20	6.00	10(broad)				
										4.81	50
						3.30	20	3.20	50	4.40	30
		3.25	10								
3.16	20			3.10	10					3.15	10
		2.40	100								
2.37	100*			2.34	100	2.37	100	2.34*	100	2.34*	100
										2.20	20
2.06	60*							2.05*	50	2.04*	75
				2.00	40	1.99	50				
1.99	10	1.97	30					1.98	20	1.98	20
1.87	20			1.88	20	1.90	40	1.90	10		
		1.85	30								
						1.61	20				
1.44	40*			1.50	10			1.43*	50	1.40*	50
		1.42	50								

*Aluminum

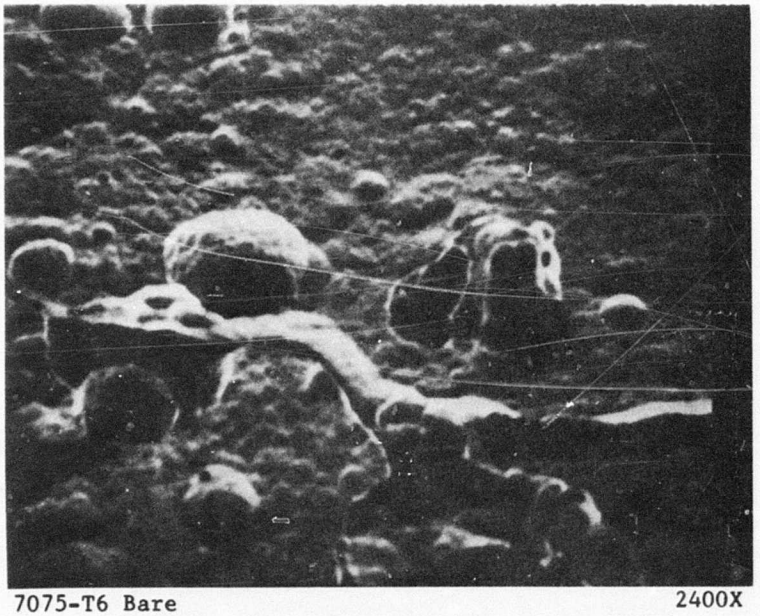
Figures 5, 6, and 7 are straight SEM photos of the sulfuric acid low voltage anodized at 1.0 VDC for 30 seconds. As clearly shown in Figure 5, the surface is characteristic of the "as-etched" surfaces showing grain boundaries in the 7075-T6 bare aluminum. Looking closely, a fine granular appearance is evident over the surface, and in Figures 6 and 7 this granular surface becomes more apparent and characteristic of the anodic coatings.

Crystallographic characterization of the developed "oxide surfaces" or corrosion products is performed with the Hitachi HU-11A electron microscope. The specimen is placed in the lower lens position for high resolution electron diffraction reflection technique. The resulting plate is then read on a conventional rotating measurement stage. Since these oxide layers or corrosion products are grown from the bare metal outward, a great prevalence for a "single crystal" type or epitaxial growth pattern of crystallization exists.



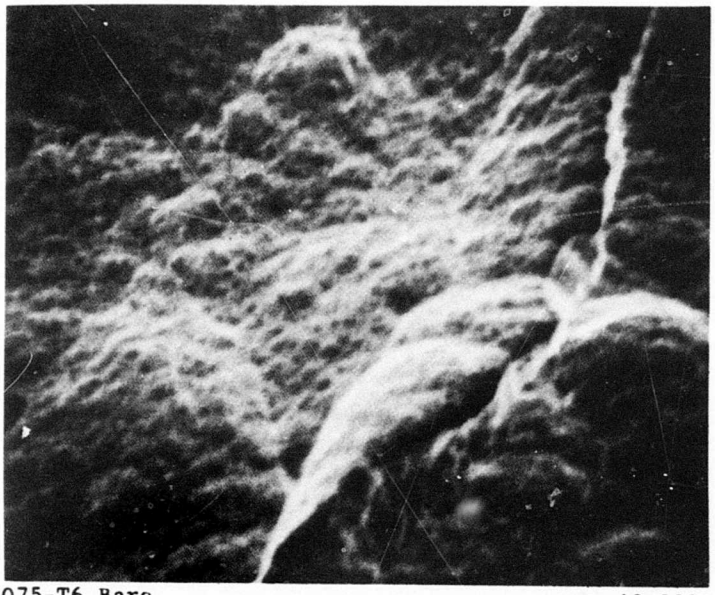
7075-T6 Bare 1000X

FIGURE 5. SEM PHOTOMICROGRAPH OF 30-SECOND LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE



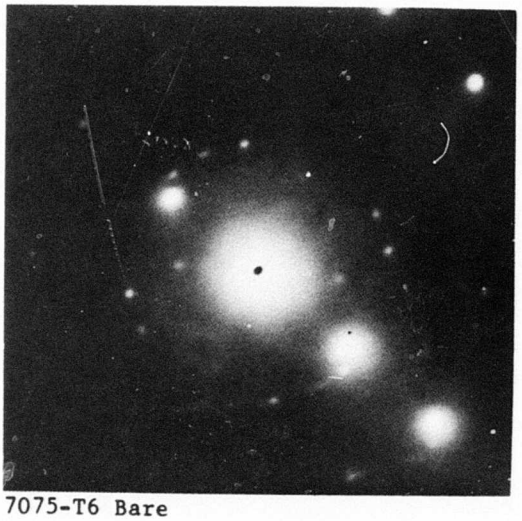
7075-T6 Bare 2400X

FIGURE 6. SEM PHOTOMICROGRAPH OF 30-SECOND LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE (NOTE GRANULAR PORE CONFIGURATION ON SURFACE)



7075-T6 Bare 10,000X

FIGURE 7. SEM PHOTOMICROGRAPH OF 30-SECOND LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE (NOTE PORE STRUCTURE)



7075-T6 Bare

FIGURE 8. ELECTRON DIFFRACTION PATTERN OF 30-SECCND LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE

Thus, the resulting diffraction patterns vary from complete spot (single crystal type) to continuous ring patterns (grain size 10^{-4} to 10^{-5}mm).

The electron diffraction pattern for the sample shown in Figure 6 or 7 is shown in Figure 8. "d-spacing" analysis of the pattern revealed the presence of $\alpha Al_2O_3 \cdot H_2O$ on the surface. The pattern showed the characteristic strong lines (6.11Å, 3.16Å, 2.346Å) in the form of a spotty pattern. The primary orientation is represented by the series of diffraction spots and is in the (111) planar direction. The spotty perferably oriented pattern will indicate a relatively thin layer (<1000Å).

Figure 9 shows the coating obtained after anodizing for 5 minutes at 1.0 VDC. This photo clearly shows a typical anodic coating uniform over the entire surface including coverage of the grain boundaries normally left by etching. Electron diffraction (Figure 10) shows the presence of $\alpha Al_2O_3 \cdot H_2O$. Only in this case, the layer is approaching a polycrystalline condition. This is evidenced by the nearly continuous diffraction rings. Apparently the oxide layer is developing polycrystallinity as the thickness developes. In this case, the relative thickness would approach 5000Å to 7000Å in thickness.

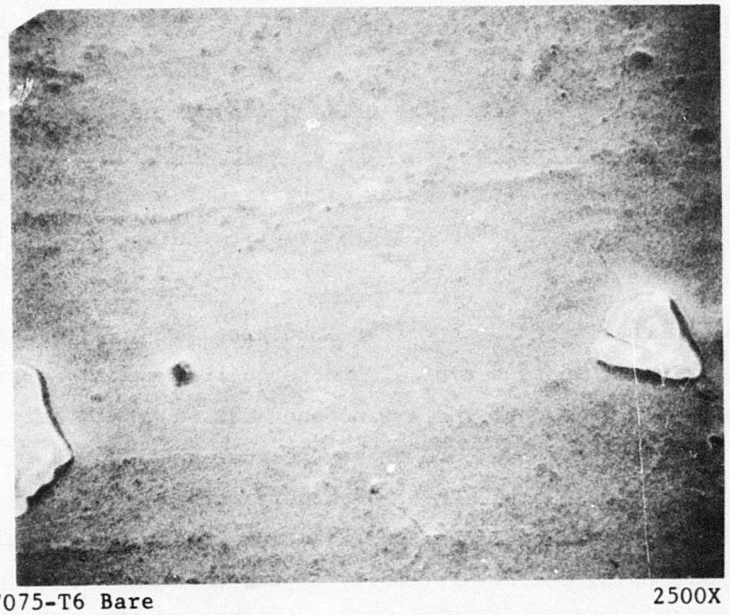
Figure 11 shows the 90° view of the 2024 and 7075 bare phosphoric acid anodize surface. The barrier type oxide is apparent with no indication of cracking. After 180° bend, the oxide has fractured and flowed with the deformed metallic surface. This is seen in Figure 12. The clad surface of both 2024 and 7075 showed a porous type oxide, Figure 13.

The low voltage, sulfuric acid anodize surface showed random cracking over the 90° bend surface, Figure 14. The surface was indicative of a sealed porous surface. The 180° bend specimen showed a very tenacious layer approaching the thickness of the phosphoric acid anodized surface, Figure 15.

As a means of relative thickness comparison, a standard FPL etch surface was also examined at 90° and 180° bend. This is shown in Figure 16. The FPL oxide appears as thin particles floating on the metallic substrate.

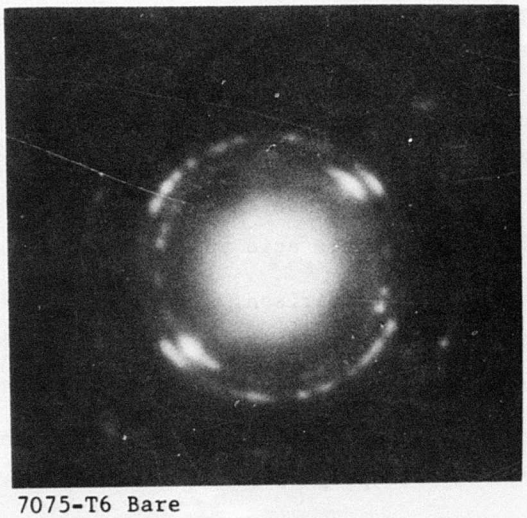
Table II shows a summary of various physical and crystallographic characteristics of these three surface preparations.

Figure 17 shows the character of the oxide on the ammonium tartrate anodized 2024 and 7075 bare surfaces. Figure 18 shows the microstructure of the ammonium tartrate anodize for 5 minutes at 1, 2, 3, and 4 volts. The



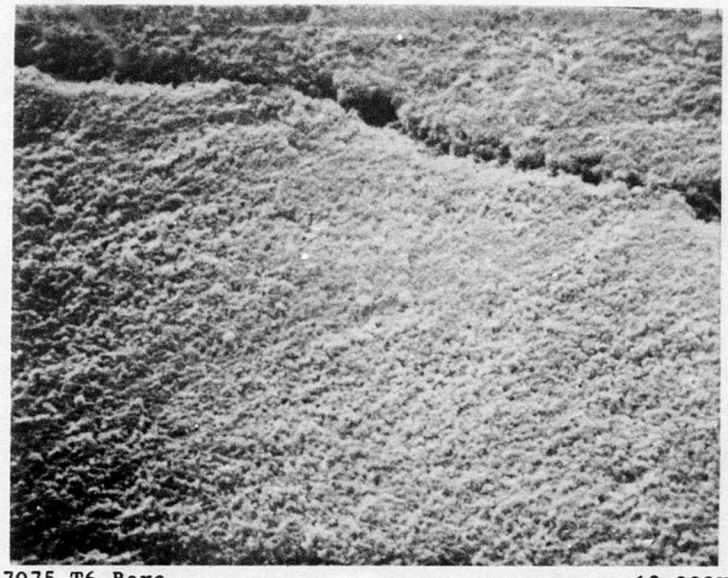
7075-T6 Bare 2500X

FIGURE 9. SEM PHOTOMICROGRAPH OF 5-MINUTE LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE



7075-T6 Bare

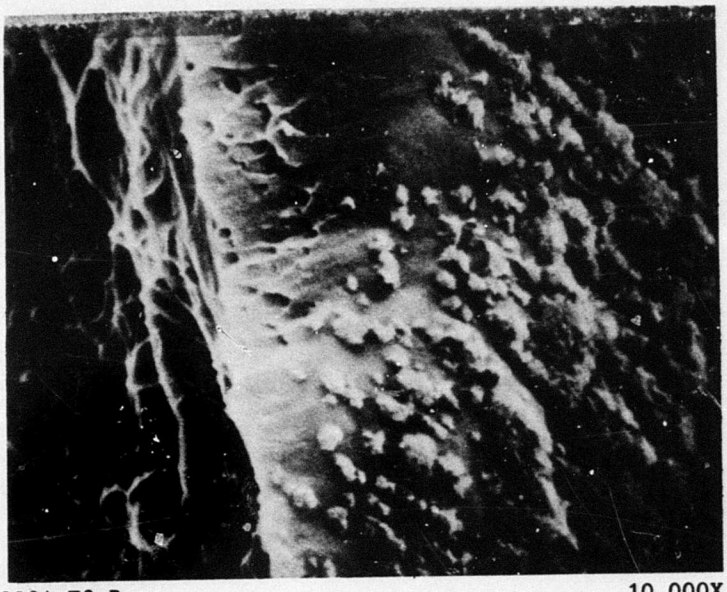
FIGURE 10. ELECTRON DIFFRACTION PATTERN OF 5-MINUTE LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE



7075-T6 Bare 12,000X

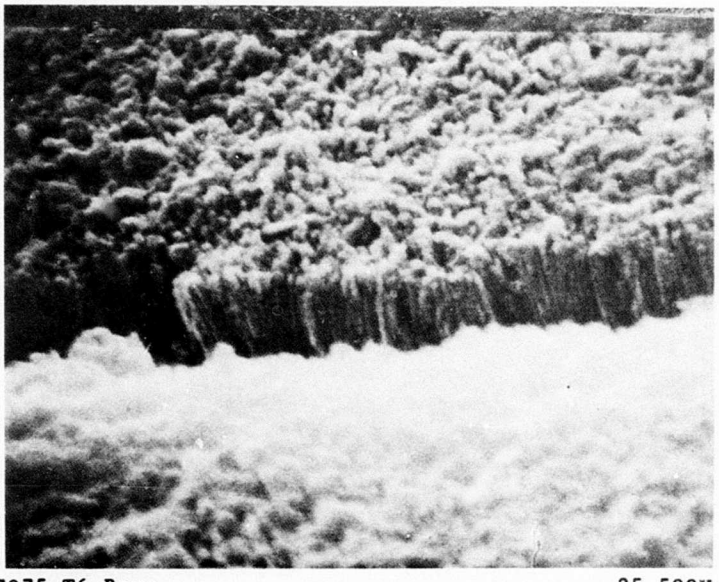
2024-T3 Bare 12,300X

FIGURE 11. SEM PHOTOMICROGRAPH OF PHOSPHORIC ACID ANODIZE SURFACE BENT 90°

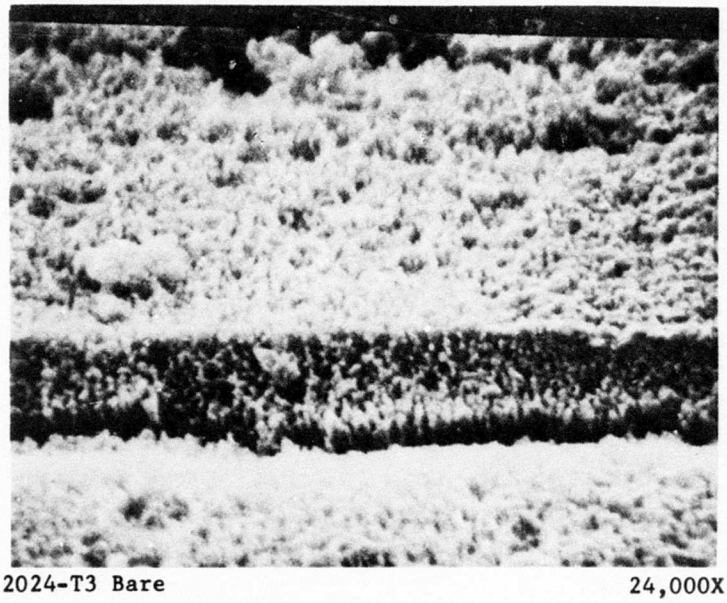


2024-T3 Bare 10,000X

FIGURE 12. SEM PHOTOMICROGRAPH OF PHOSPHORIC ACID ANODIZE SURFACE BENT 180°

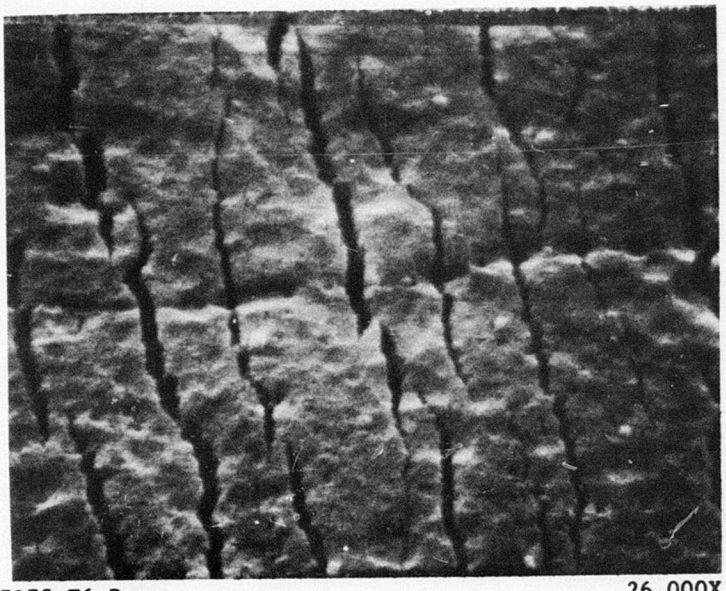


7075-T6 Bare 25,500X

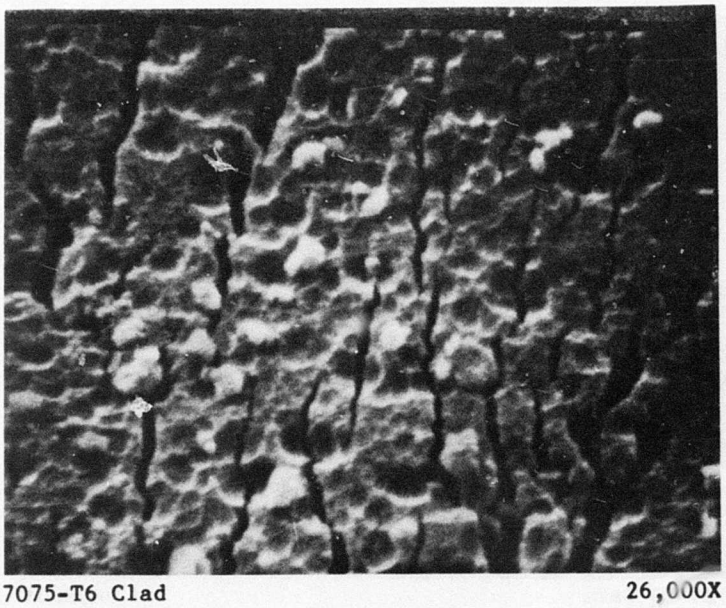


2024-T3 Bare 24,000X

FIGURE 13. SEM PHOTOMICROGRAPH OF PHOSPHORIC ACID ANODIZE SURFACE BENT 90°



7075-T6 Bare 26,000X



7075-T6 Clad 26,000X

FIGURE 14. SEM PHOTOMICROGRAPH OF LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE BENT 90°

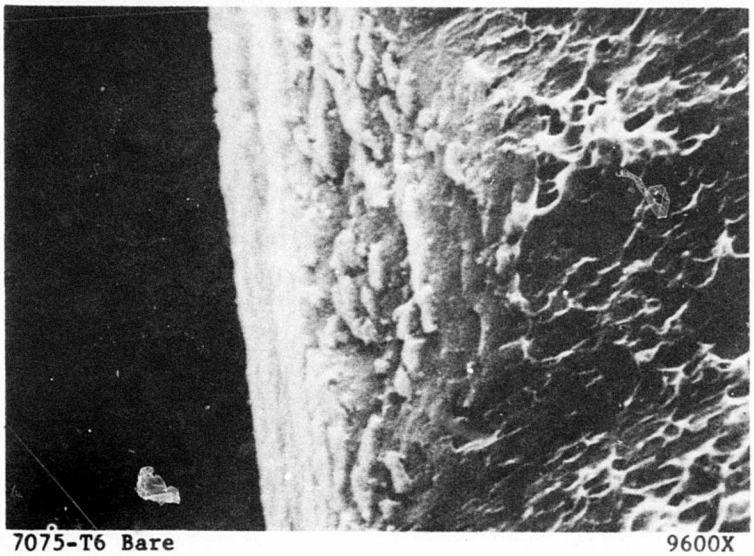
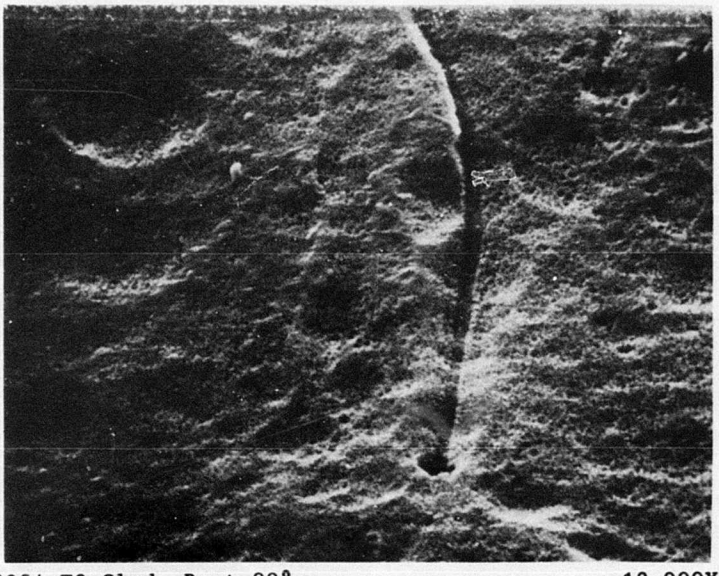
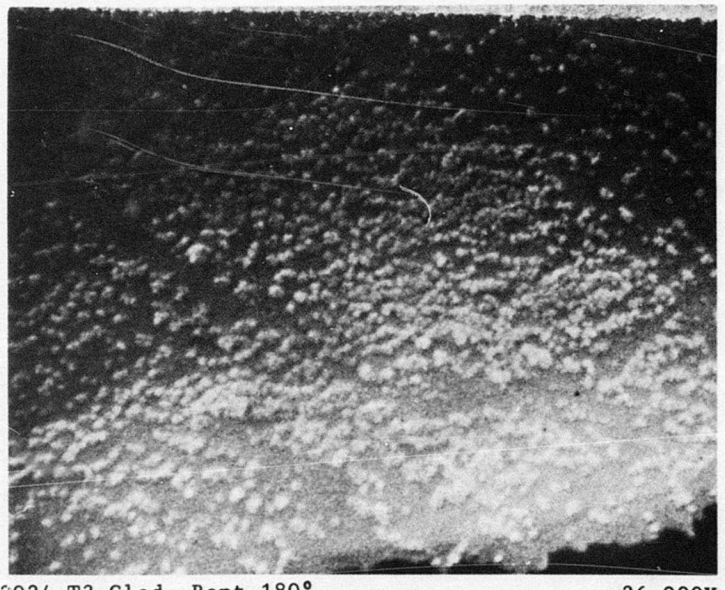


FIGURE 15. SEM PHOTOMICROGRAPH OF LOW-VOLTAGE SULFURIC ACID ANODIZE SURFACE BENT 180°

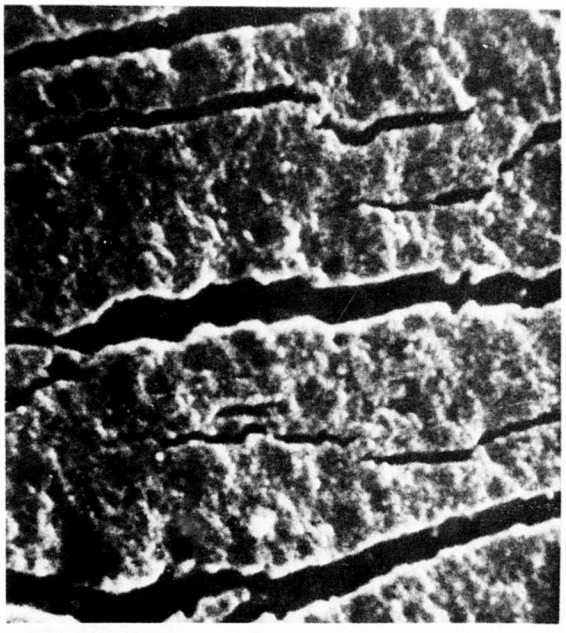


2024-T3 Clad Bent 90° 12,000X

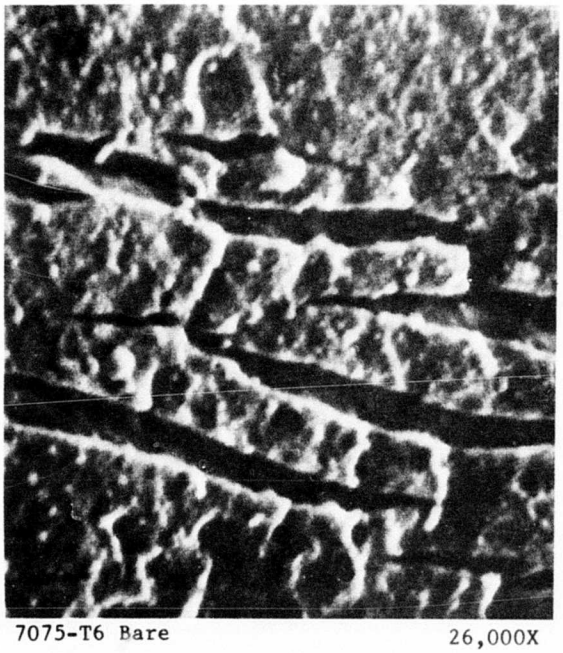


2024-T3 Clad Bent 180° 26,000X

FIGURE 16. SEM PHOTOMICROGRAPH OF FPL ETCH SURFACE

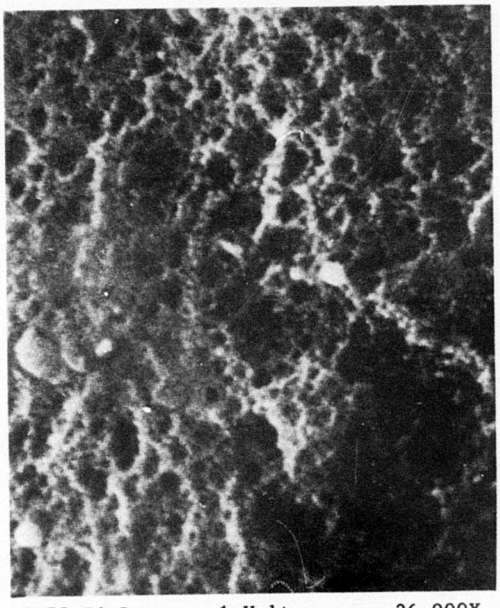


2024-T3 Bare 26,000X

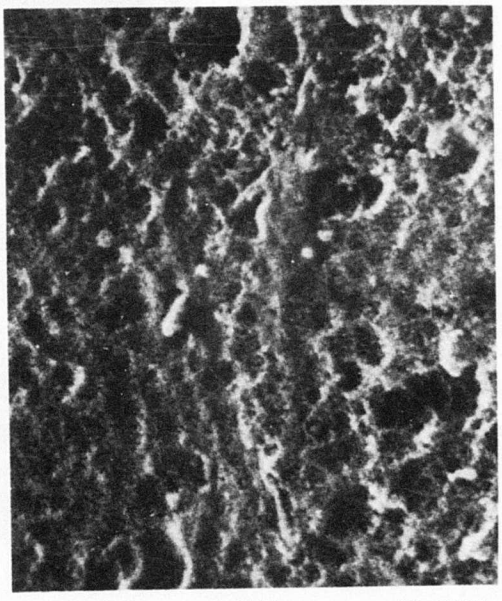


7075-T6 Bare 26,000X

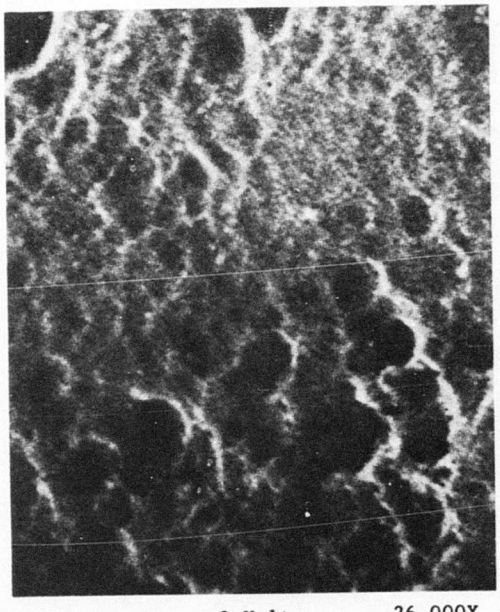
FIGURE 17. SEM PHOTOMICROGRAPH OF 10-MINUTE-40-VOLT AMMONIUM TARTRATE ANODIZE SURFACE BENT 90°



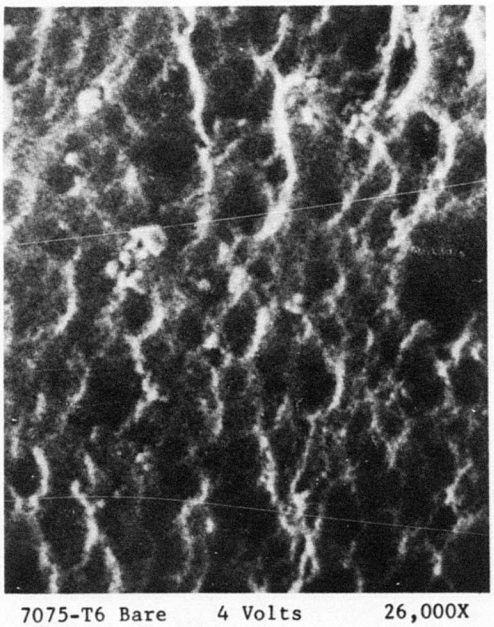
7075-T6 Bare 1 Volt 26,000X



7075-T6 Bare 2 Volts 26,000X



7075-T6 Bare 3 Volts 26,000X



7075-T6 Bare 4 Volts 26,000X

FIGURE 18. SEM PHOTOMICROGRAPHS OF 5-MINUTE-1, 2, 3, & 4 VOLT AMMONIUM TARTRATE ANODIZE SURFACES BENT 90°

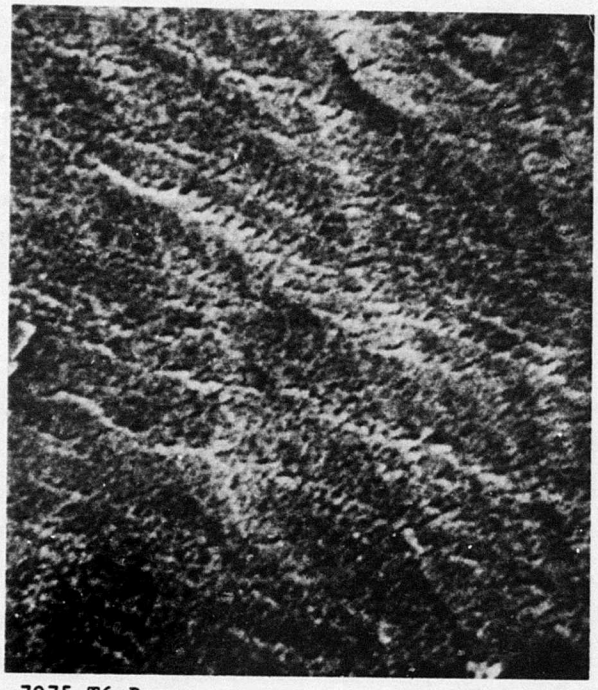
increased growth in pore size is evident. Figure 19 shows the surface studies of a 90° bend specimen of FPL etch/dichromate sealed for 80 minutes.

In order to evaluate the step-by-step process of preparing FPL surfaces, several series of 7075-T6 bare were examined after vapor degreasing, alkaline cleaning, deoxidizing and FPL etching. Figures 20 through 27 show two different runs through the complete process. Comparison of the photomicrograph indicated that the processes were treating the surfaces identically. They were reproducible.

Failure Analysis

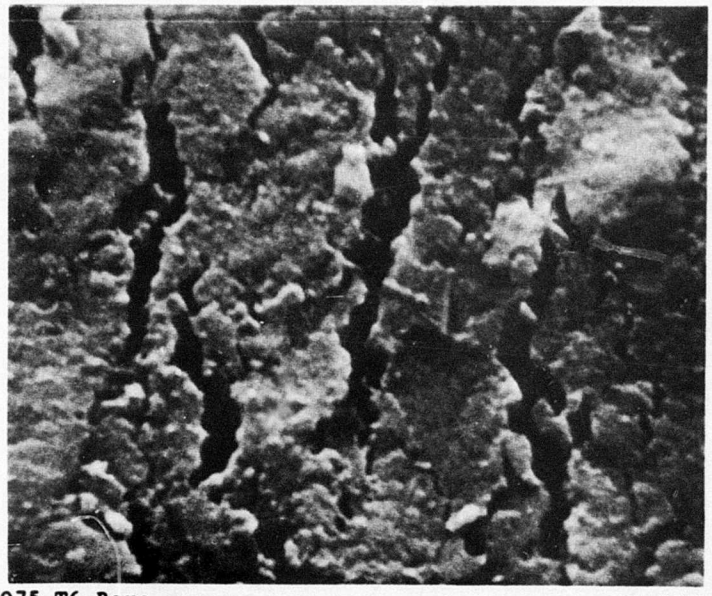
Additional work has also been performed to evaluate the degradation mechanism of adhesives bonded to an FPL etch prepared aluminum surface exposed to a humid atmosphere. It is assumed that the FPL etch produces a thin, relatively stable, and relatively porous $\alpha Al_2O_3 \cdot H_2O$ layer on the aluminum surface. It is also assumed that the adhesive layer acts as an absorbent layer to the moisture atmosphere and that the absorbed moisture in the adhesive layer reacts with the metal interface to hydrolyze the sub-oxide layer causing the growth of aluminum hydroxides. It is then hypothesized that the metal/oxide interface layer fails under a stressed/humidity exposure at the time that the hydroxide layer becomes thick enough and consequently weak enough to no longer support the applied load.

The first test of this hypothesis was conducted as described below. First, to determine the hydrolysis action assumed above, two specimens of 7075-T6 alclad aluminum, .064" x 1" x 5", were prepared by processing through the standard FPL etch procedure. One of these specimens was subjected to a 24-hour exposure to stress and 100% R.H. at 120F using the simple bend loading apparatus shown in Figure 28. The other specimen was used as a control. Both specimen surfaces were characterized by SEM and electron diffraction. Figure 29 shows the control surface and Figure 30 shows the 24-hour exposed surface. Beta oxide crystals can be seen forming around



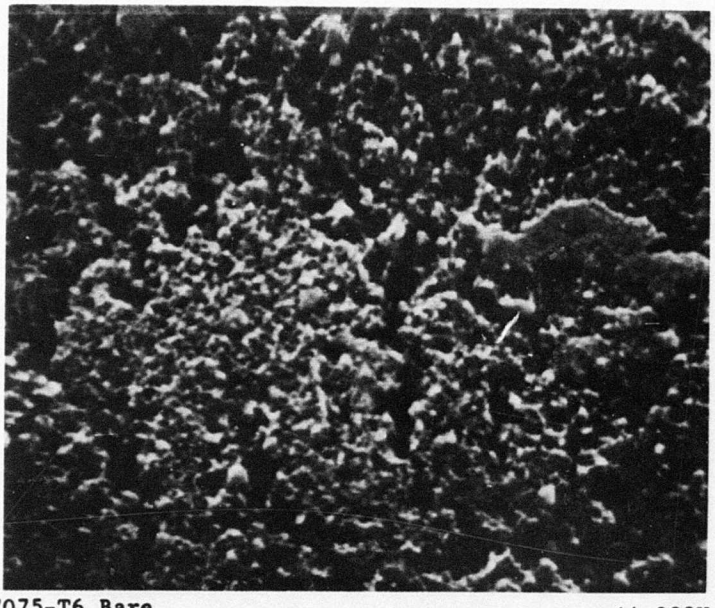
7075-T6 Bare 26,000X

FIGURE 19. SEM PHOTOMICROGRAPH OF FPL ETCH/ 80-MINUTE DICHROMATE SEALED SURFACE, BENT 90°



7075-T6 Bare 14,000X

FIGURE 20. AS-RECEIVED, VAPOR DEGREASED, RUN 1

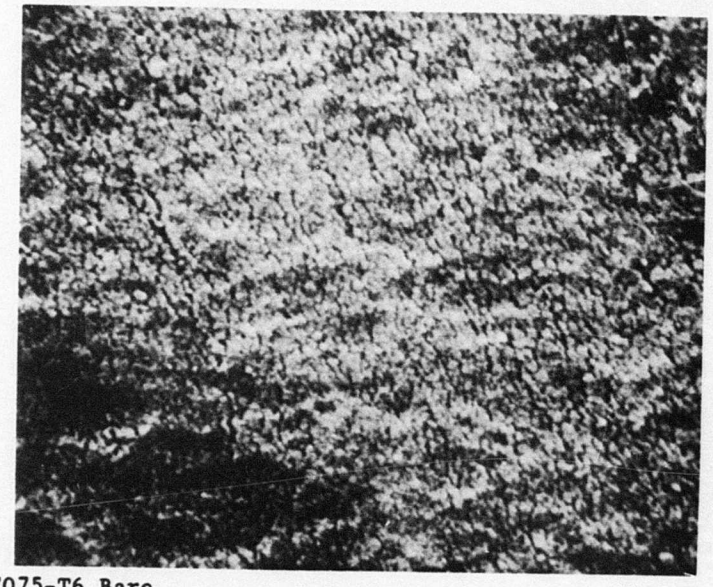


7075-T6 Bare 14,000X

FIGURE 21. ALKALINE CLEANED, RUN 1

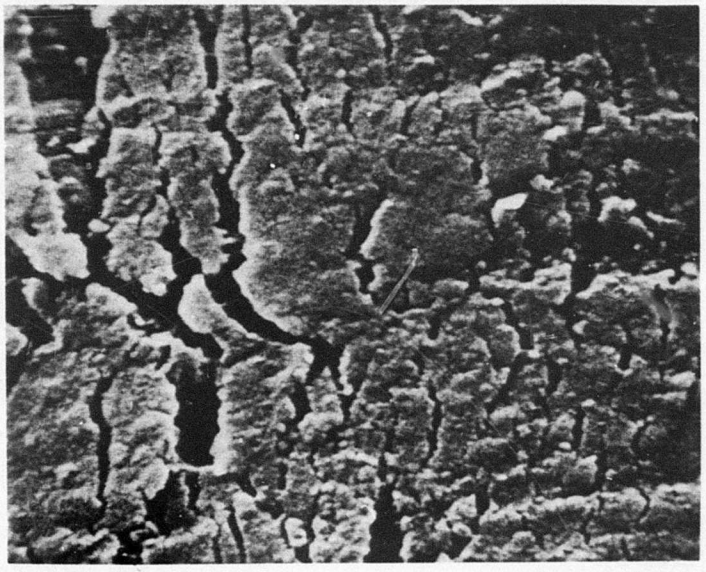
7075-T6 Bare 14,000X

FIGURE 22. DEOXIDIZED, RUN 1



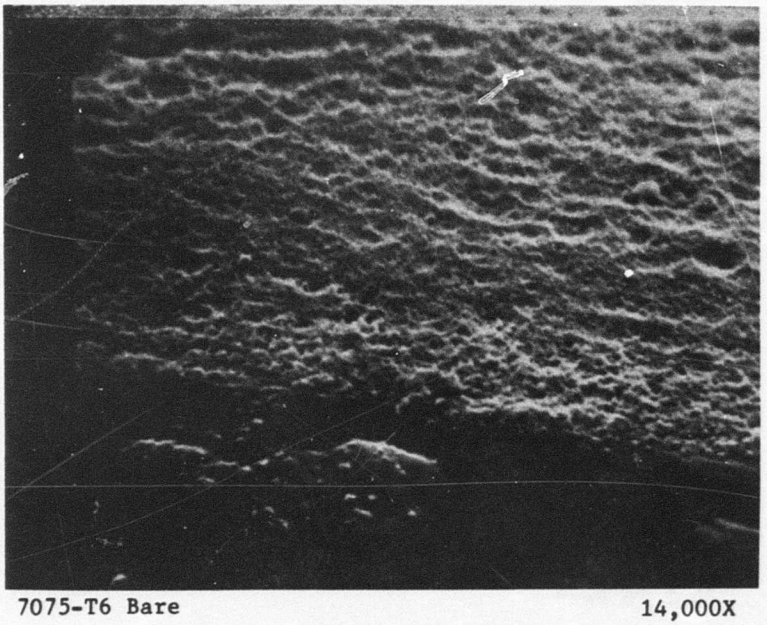
7075-T6 Bare 14,000X

FIGURE 23. FPL ETCHED, RUN 1



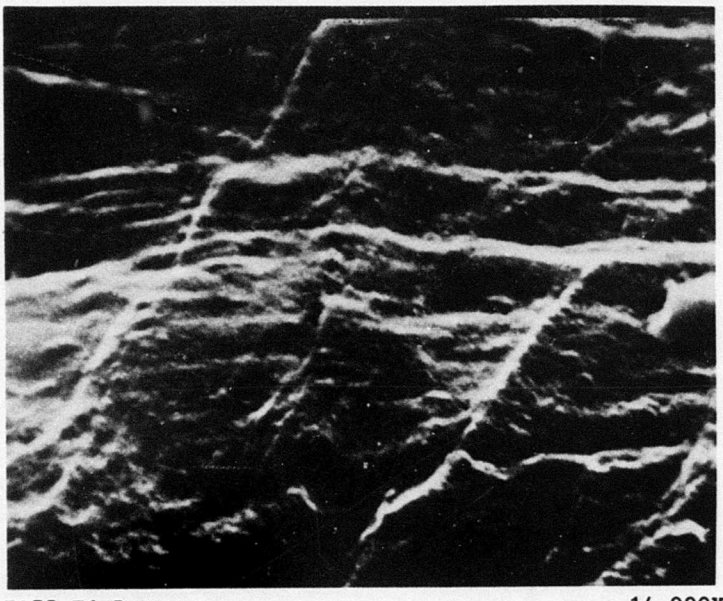
7075-T6 Bare 14,000X

FIGURE 24. AS-RECEIVED, VAPOR DEGREASED, RUN 2



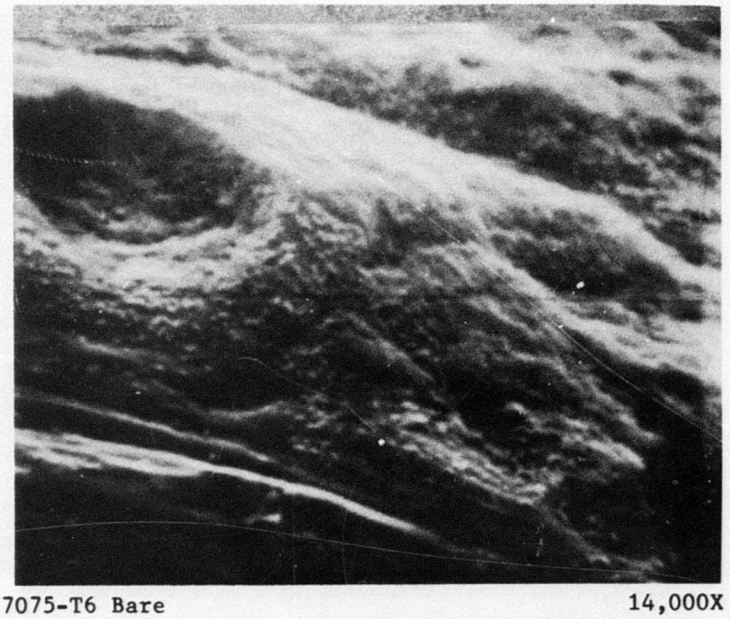
7075-T6 Bare 14,000X

FIGURE 25. ALKALINE CLEANED, RUN 2



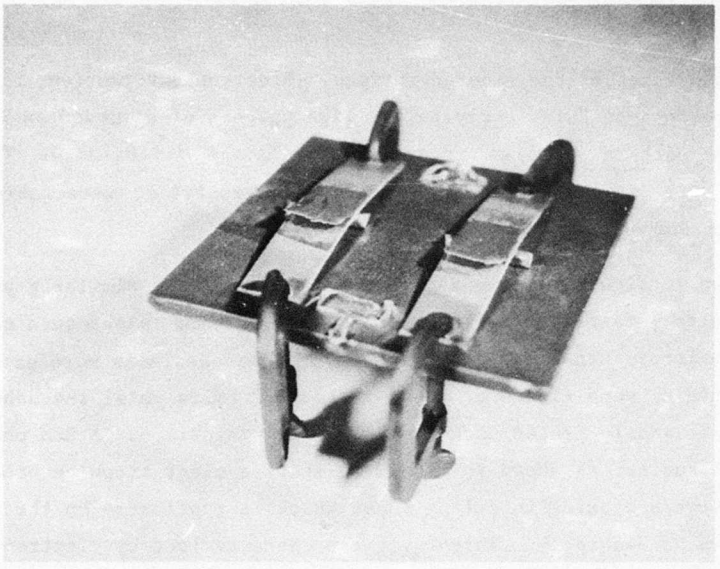
7075-T6 Bare 14,000X

FIGURE 26. DEOXIDIZED, RUN 2



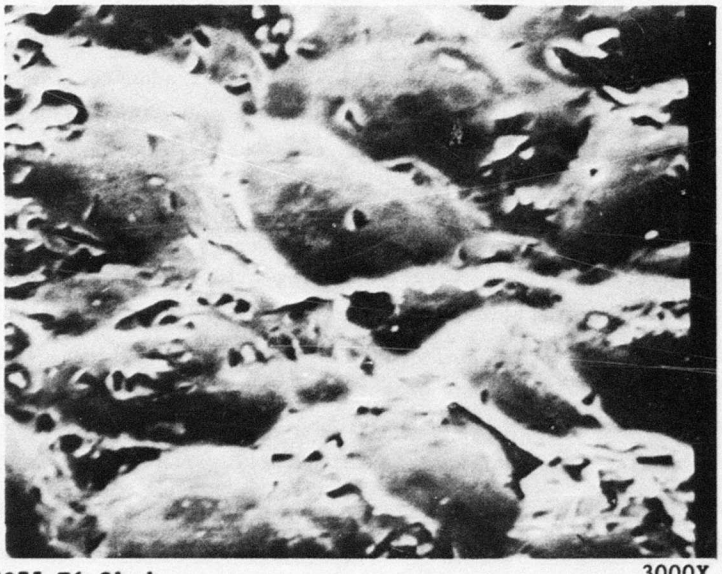
7075-T6 Bare 14,000X

FIGURE 27. FPL ETCHED, RUN 2



1/4X

FIGURE 28. MACROPHOTOGRAPH OF TEST JIG FOR STRESSED EXPOSURE TESTING



7075-T6 Clad

3000X

FIGURE 29. SEM PHOTOMICROGRAPH OF FPL ETCH SURFACE, CONTROL

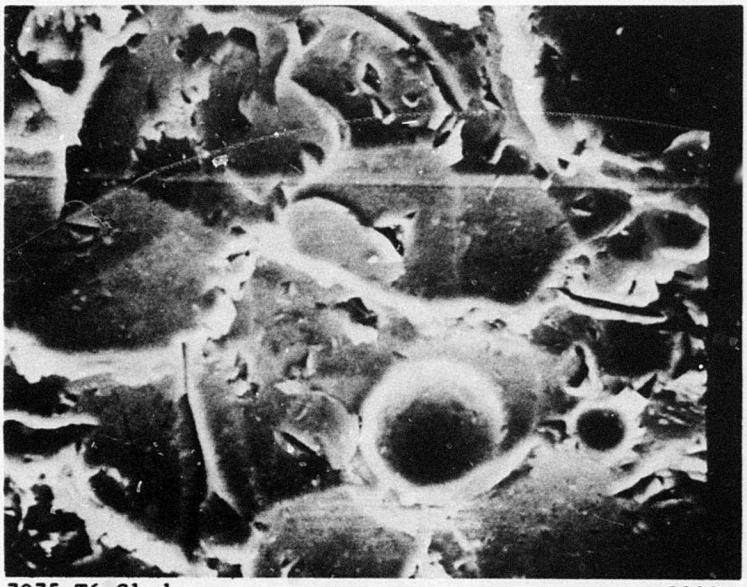
the grain boundaries of the exposed surface. Electron diffraction (Figure 31 shows the presence of "single crystal" - like patches of compound on the surface. The pattern was read and analyzed to be the $\beta Al_2O_3 \cdot 3H_2O$. The pattern was very diffuse and spotty probably as a result of metastable conditions of compound formations.

As shown in Figure 28, two additional specimens were similarly prepared and coated with a fairly thick layer of EC-2216, a room temperature curing, relatively moisture sensitive, epoxy system. These specimens were exposed to the same humidity conditions for approximately 60 hours until the adhesive layer could be easily peeled back from the metal interface. A SEM photograph of the metal surface as shown in Figure 32 shows a clear stepwise break in the metal oxide/hydroxide interface layer which is replicated on the adhesive side as shown in Figure 33. This layer now characterized by electron diffraction shows (Figure 34) the presence of $\alpha Al_2O_3 \cdot H_2O$ and $\beta Al_2O_3 \cdot 3H_2O$. The faint diffuse background pattern was read and identified to be the αAl_2O_3. The scattered diffraction spots were analyzed to be best fitted to the $\beta Al_2O_3 \cdot 3H_2O$ crystal structure.

These data show the formation of the hydroxide on the prepared surface due to the moisture exposure and the failure of that hydroxide layer when the adhesive is removed after exposure. The ease of adhesive removal and hydroxide layer failure plus the lack of obvious corrosion products (visible) on the interfacial surface tend to support the above hypothesis that hydration weakens the oxide layer.

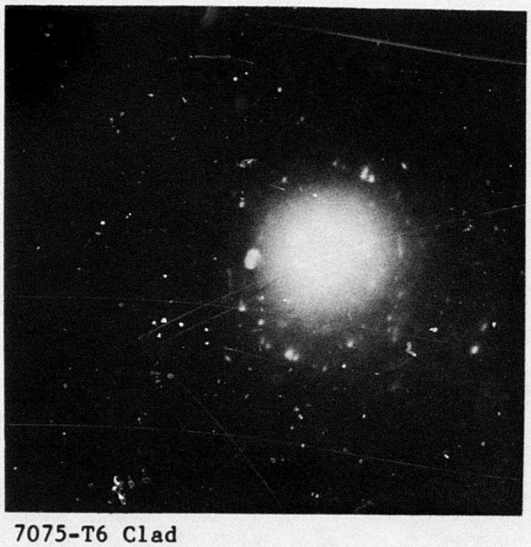
Our metal interface work also tends to confirm literature evidence to the effect that bayerite is the naturally forming oxide on the aluminum surface under a combination of applied stress, humidity, and time of exposure. Additional experimentation was conducted using standard durability tests and examination of the failure interfaces after exposure. Each of the interfaces examined showed bayerite on the adhesive and on the aluminum surfaces tending to confirm the fracture occurrence in the oxide layer.

Since the stability or "shelf life" of a prepared surface has a great bearing on its usefulness as a production preparation method, shelf life physical and crystallographic character was investigated. Surfaces of 7075-T6 bare were prepared by three processes as follows:



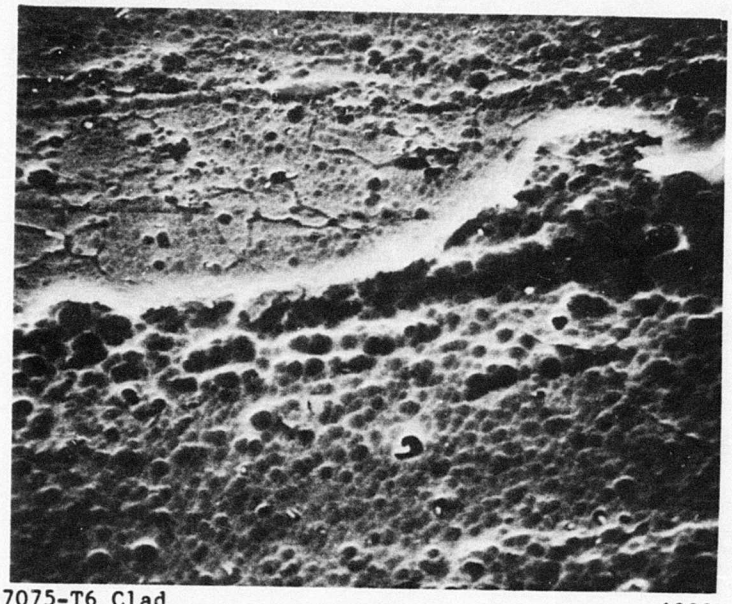
7075-T6 Clad 3000X

FIGURE 30. SEM PHOTOMICROGRAPH OF FPL ETCH SURFACE AFTER 24-HOUR EXPOSURE (NOTE PHASE FORMING AT EDGES OF GRAIN BOUNDARIES)



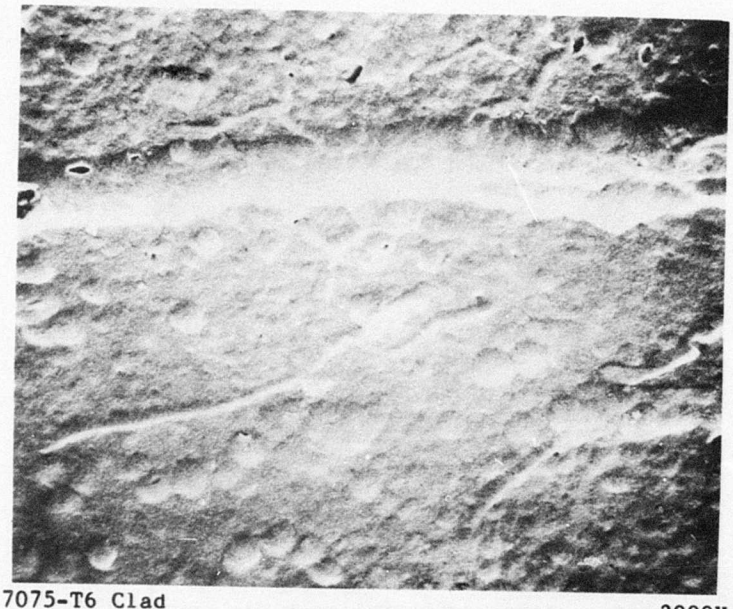
7075-T6 Clad

FIGURE 31. ELECTRON DIFFRACTION PATTERN OF GRAIN BOUNDARY CONSTITUENT SHOWN IN FIGURE 28



7075-T6 Clad 1000X

FIGURE 32. SEM PHOTOMICROGRAPH OF STEP BREAK IN METAL OXIDE/HYDROXIDE INTERFACE LAYER



7075-T6 Clad 2000X

FIGURE 33. SEM PHOTOMICROGRAPH OF ADHESIVE SIDE OF FAILURE

FIGURE 34. ELECTRON DIFFRACTION OF SURFACE RETAINED ON ADHESIVE SIDE FROM FIGURE 33

1. FPL etch
2. FPL etch/dichromate sealed, 90 minutes
3. Ammonium tartrate anodize, 4 volts

Specimens were examined at 90° bends after room temperature exposures (72F @ 50% R.H.) of 1, 4, 8, 24, 48, 72, 100, 150, and 200 hours. The following conclusions were obtained:

1. In no instance did a physical change appear in any of the three surfaces;
2. At 25 hours, the FPL surface showed the presence of $\beta Al_2O_3 \cdot 3H_2O$ (bayerite) in addition to $\alpha Al_2O_3 \cdot H_2O$ (boehmite);
3. At 72 hours, a line broadening of the basic $\alpha Al_2O_3 \cdot H_2O$ diffraction pattern occurred in the FPL/dichromate sealed specimen. No further changes occurred through 200 hours to 300 hours;
4. No changes occurred in the boehmite structure of the ammonium tartrate anodize through the 200-hour exposure.

These studies show the inherent weakness of porosity of the FPL etched surface in that the surface will react to a moist atmosphere in a relatively short period of time to form a loosely adhering bayerite oxide layer. This layer is forming at the oxide/metal interface and growing around the boehmite layer in place. They also show the stability of the anodized surfaces in exposure to the same ambient atmospheric conditions.

A model concept of the interface between the adhesive and the aluminum substrate can now be defined in fairly broad terms. This concept is depicted in Figure 35 and shows the various interaction zones and oxide layers which exist in the interface. One mode of adhesion failure, as discussed above, occurs in zone 3 under a combination of stress and moisture. Other modes of failure can also be described in terms of the model concept.

Conclusions

Through these studies the following relevant conclusions may be drawn:

a. All of the anodizing procedures and the hot water/dichromate seal procedures produce a relatively thin, continuous, highly adherent layer of boehmite ($\alpha Al_2O_3 \cdot H_2O$) on each of the aluminum alloy surfaces. This represents experimental reconfirmation of the literature references.

b. Thickness of the oxide layer is easily controlled by use of "barrier layer" anodizing techniques. However, the oxide layer thickness and character throughout the thickness has not been completely defined. Additional studies need to be conducted in this area.

c. The technique of bending the surface to fracture the oxide layer is essential to using the SEM for accurate determination of the existence and character of the layer.

PHASE II - ADHESIVE MODIFICATION

This phase of the program was designed to evaluate the addition of corrosion inhibiting agents to standard adhesive formulations to determine the effect of such additives on the static strengths, weldability and durability of the resultant joint. In accordance with literature and experience, zinc and strontium chromate are the most conventional additives for corrosion inhibition due to their very slight solubility and effective corrosion protection. Consequently, finely divided (100-200 mesh) CP powders of zinc and strontium chromate were selected for the initial modification experiments. These powders were added to the Goodrich A-1396B adhesive system in ratios of 5 PHR, 10 PHR, and 15 PHR. Standard lap shear panels were fabricated to evaluate the static strengths of the joints at room temperature, 180F, and room temperature after 30-day salt spray exposure. The results of these tests are contained in Table V.

For this phase of the program, three "off-the-shelf" adhesives were evaluated. These were B.F. Goodrich A-1396B, Hysol 9312, and chromated Hysol EA-9312. The Goodrich adhesive gave the better results and the Hysol adhesives were satisfactory initially. However, subsequent lots of the Hysol adhesive were completely different from the original lot and the original lot could not be reproduced by the manufacturer in time for use on this program. Therefore, the Hysol adhesives were dropped from the program.

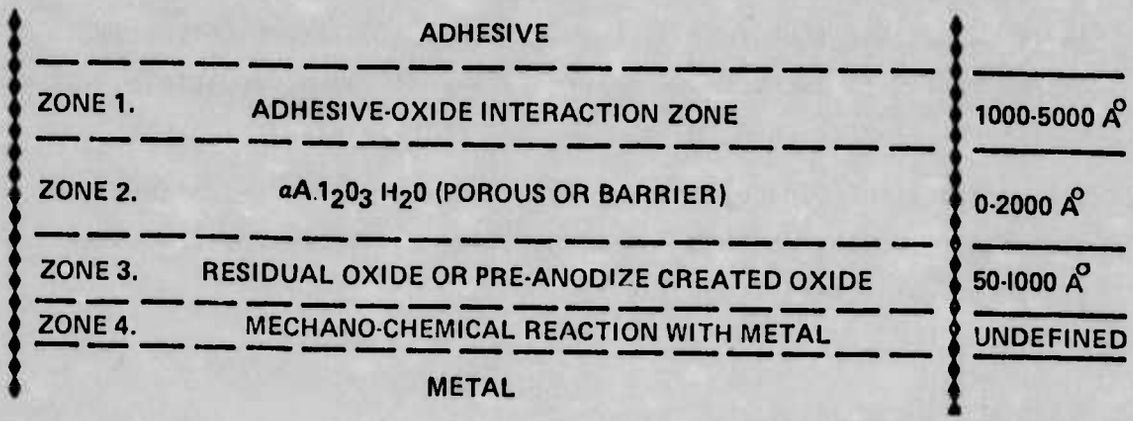


FIGURE 35. INTERFACIAL ZONE MODEL

TABLE V
STATIC STRENGTHS OF CHROMATE MODIFIED
A-1396B ADHESIVE ON 7075-T6 BARE ALUMINUM

Panel	Additive	Lap Shear Strength* (PSI)	
		Room Temperature	180F
1	Control	3790	2230
2	5 PHR** $ZnCrO_4$	4020	2670
3	10 PHR $ZnCrO_4$	4170	2650
4	15 PHR $ZnCrO_4$	4080	2550
5	5 PHR $SrCrO_4$	4430	2370
6	10 PHR SrCrO	4510	2550
7	15 PHR SrCrO	4370	2790
30-Day Salt Spray Exposure			
1	Control	3900	
2	5 PHR $ZnCrO_4$	3760	
3	10 PHR $ZnCrO_4$	3330	
4	15 PHR $ZnCrO_4$	3020	
5	5 PHR $SrCrO_4$	3860	
6	10 PHR $SrCrO_4$	3850	
7	15 PHR $SrCrO_4$	3740	

*Note: Reported values are the average of five specimens each.

**PHR = Parts per Hundred Resin

The 30-day salt spray exposure tests show no or only slight degradation of the unmodified and the modified adhesives. However, the strength levels after exposure are higher with the strontium chromate than with the zinc and, also, with zinc chromate the trend tends to lower strengths with increasing percentages of additive. Therefore, strontium chromate was selected for further modification studies and the lower percentage levels were evaluated in stress corrosion tests.

The specimens tested in Table V were made with vacuum bag (15 psi) pressure. Samples were placed in a cold oven, heated to 250F, and cured at 250F for 1 hour. Results were lower than anticipated. This has been attributed to "adhesive starving" in the bond area because of the 15 psi pressure and the low viscosity of the adhesive. "Dead weight" (1.5 psi) pressure and Cab-O-Sil to control flow have resulted in bond strength improvements of 1000 to 1500 psi.

Additional modification of the A-1396B adhesive has been necessary to control flow of the system when cured on an inclined or vertical surface. This has been accomplished by the addition of Cab-O-Sil to a percentage level of about 7 percent. The primary formulation selected for Phase III characterization at present is:

Modified Goodrich A-1396B

A-1396B	-	90%
Cab-O-Sil	-	7%
$SrCrO_3$	-	3%
		100%

This formulation has been tested in lap shear to compare initial strengths with the unmodified adhesive. These lap shears were cured using lead weight pressures of about 1 psi.

Test results are as follows: 5520 psi average of five specimens for the unmodified A-1396B, 5360 psi average for the modified version. These values confirm the requirement for low pressure curing, show the maintenance of strength after modification, and are representative of weld-bonded strength levels. No difficulty has been encountered in welding through the modified formulation.

This formulation was provided to B.F. Goodrich and is now being supplied by that company under the trade designation of 0500-PE-130. Subsequent testing under this program has been conducted with the manufacturer's product.

DEVELOPMENT OF WELDING PARAMETERS

General Procedures

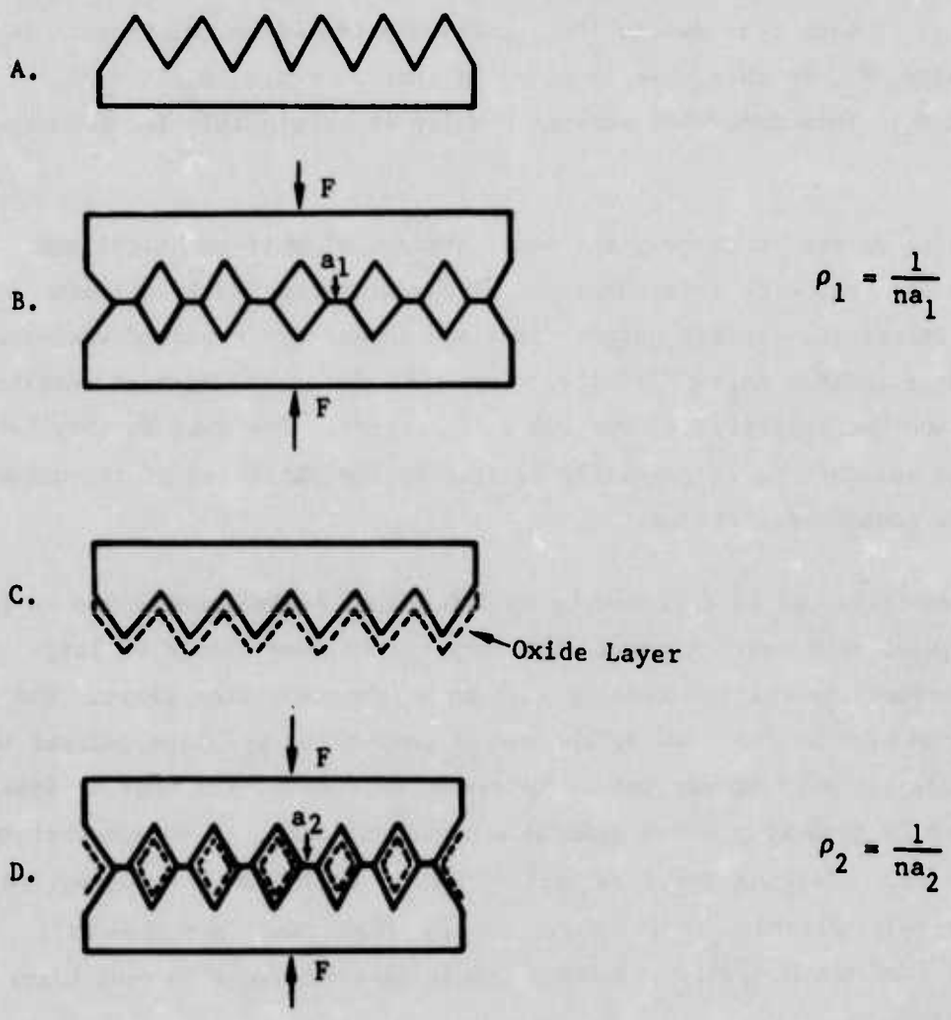
Sheared and deburred aluminum blanks were surface treated with various solutions: spot-weld etch, FPL etch, and FPL etch plus dichromate seal. The treatment procedures and solution compositions are shown in Appendix I.

In the beginning, standard welding schedules for 0.063-inch thick bare 7075-T6 aluminum were used to weld material cleaned with the spot-weld etch and FPL etch without adhesive. For each surface treatment, a plot of strength versus welding current was obtained by increasing welding current from low to high values until expulsion took place. At the current level which produces expulsion, the tension-shear strength should be above 900 lbs. This provides sufficient latitude for reducing the welding current to eliminate expulsion and still achieve adequate strength. If premature expulsion was encountered, the welding parameters were then re-adjusted by increasing electrode-forge force or up-slope time, or both.

For each surface-treated aluminum alloy, curves of joint strength and electrode indentation versus welding current were plotted for varying electrode forces. The recommended welding schedule was the one that permitted the widest welding current range between the low current value which produced the minimum joint strength (670 lbs. for 0.063-inch sheet) specified in MIL-W-6858 and the high current value which produced a maximum electrode indentation of 10% without expulsion.

Technical Discussion

The problems encountered in weldbonding of durable surfaces can be illustrated by considering a simplified model as described as follows: the surface finish of a rolled aluminum sheet is microscopically rough, as shown in Figure 36. The surface in Figure 36(A) is oxide-free, having uniformly distributed peaks and valleys. When an electrode force is applied to the sheets, Figure 36(B), plastic deformation takes place at the contact peaks, each of which has an area equal to a_1. If the welding current is 1 ampere and there are n peaks under the electrodes, then the current density $\rho_1 = 1/na_1$. After surface treatment, a layer of oxide covers the peaks and valleys, as shown in Figure 36(C). When two surface-treated sheets are placed between the electrodes,



$$\rho_1 = \frac{1}{na_1}$$

$$\rho_2 = \frac{1}{na_2}$$

where $a_1 >> a_2$. Therefore $\rho_2 >> \rho_1$

where: a_1 and a_2 are areas without and with oxide layer, respectively

and, ρ_1 and ρ_2 are current densities in the areas a_1 and a_2, respectively.

FIGURE 36. MODEL OF SURFACE CONTACT RESISTANCE

the oxide layer cracks at the peaks under pressure. The peaks make metal-to-metal contact again, as shown in Figure 36(D). The area of contact for each peak, a_2, is much less due to the increased oxide layer thickness. The current density, ρ_2, in this case is equal to $1/na_2$. Hence, ρ_2 is much greater than ρ_1. This excessive current density is responsible for premature expulsion.

Of course, on real surfaces, the peaks are not of uniform height and distribution and the oxide layer does not have a microscopically uniform thickness. Therefore, erratic nugget sizes and shapes are observed whenever the oxide layer exceeds certain limits. Table VI lists the contact resistance thicknesses and "weldability" of various oxide layers. The data in this table indicate that weldability is generally related to the thickness of the oxide layer and the contact resistance.

The weldability can be improved by applying higher electrode force to increase the microscopic contact area. The increase in area should be large enough to decrease the current density well below the expulsion limit. The weldability can also be improved by the use of controlled up-slope current in such a way that the welding current is increased only after the contact areas have increased by gradual plastic deformation and melting. At an appropriate forge-delay time, a forging force is applied and is followed by a controlled down-slope welding current. Proper attention to these considerations will provide welds that are not only crack-and expulsion-free but also meet Class A strength standards.

During conventional spot welding, expulsion takes place near the end of the welding cycle due to the oversize molten nugget relative to the electrode force. The expulsion of molten metal causes instantaneous collapse of the molten nugget. The upward movement of the electrode due to thermal expansion and melting of the nugget is momentarily interrupted. This interruption of the electrode movement, as shown in Figure 37, represents the point at which expulsion occurs. If a forging force is applied to the weld at or before the onset of expulsion, it can be avoided. However, during the spot welding of durable surfaces (high contact resistance), expulsion begins early in the up-slope portion of the cycle, as shown in Figure 38.

TABLE VI
WELDABILITY, CONTACT RESISTANCE, AND OXIDE LAYER THICKNESS

SURFACE TREATMENT	CONTACT RESISTANCE, μOHMS	THICKNESS, Å	WELDABILITY RATING
FPL Etch	30-280	100-400	Good
FPL Etch Plus Dichromate Seal	80-400	400-700	Good up to 90 min. seal
Low Voltage Ammonium Tartrate Anodize	80-300	100-400	Good up to 5V,
Low Voltage Sulfuric Acid Anodize	200-500	2500	poor
Low Voltage Phosphoric Acid Anodize	200-500	2400	poor

TABLE VII
WELDING CURRENT RANGE FOR 7075-T6
BARE ALUMINUM USING SPOT-WELD ETCH

WELDING SCHEDULE	WELDING CURRENT (KA)		WELDING CURRENT RANGE (KA)	STRENGTH RANGE	
	STRENGTH ABOVE MIN. REQUIREMENT	INDENTATION EXCEEDS 10%		(LBS)	(KN)
I	18.9*	20.9	2.0	670-1010	2.95-4.49
II	19.5	22.1	2.6	670-1020	2.95-4.54
III	19.6	22.5	2.9	670-920	2.95-4.09
II + 15 Cycles Forge Delay	19.2	20.6	1.4	670-960	2.95-4.27
II + 10 Cycles Forge Delay	20.3	22.1	1.8	670-1040	2.95-4.63
II + 5 Cycles Forge Delay	20.7	23.8	3.1	670-1170	2.95-5.21

*Extrapolated

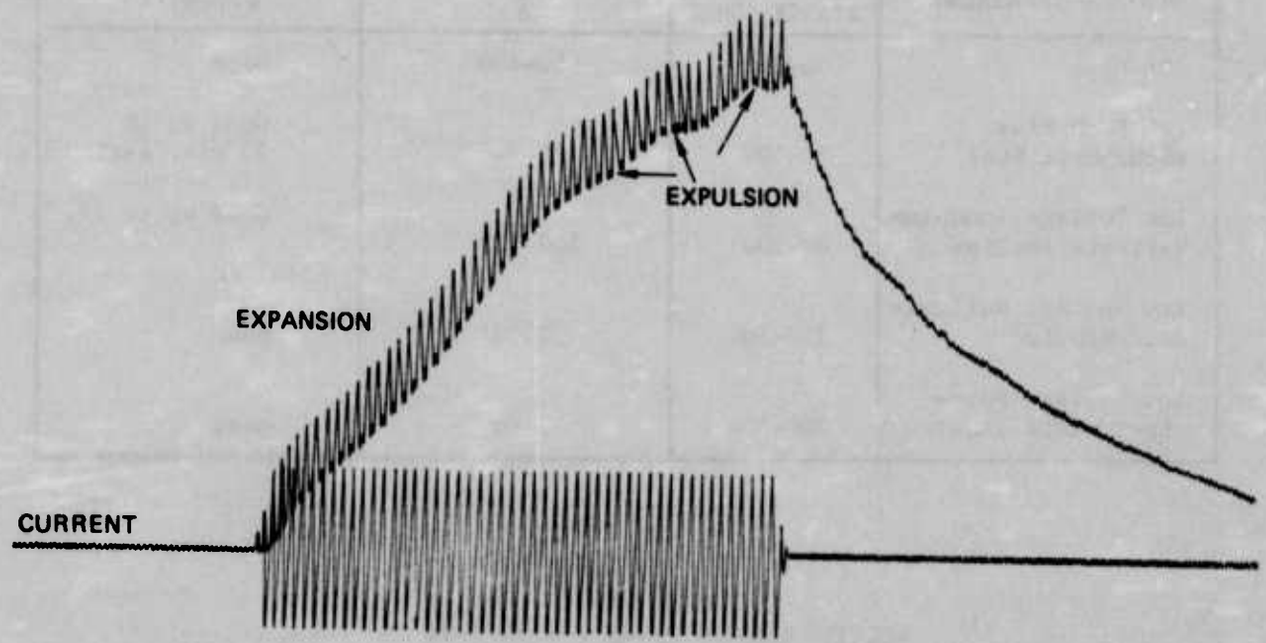


FIGURE 37. NUGGET EXPANSION TRACES SHOWING EXPULSION DUE TO HIGH CURRENT OR LOW ELECTRODE FORCE FOR LOW CONTACT RESISTANCE SURFACES WITH NO FORGE FORCE

There are three possible approaches for elimination of expulsion. One is to increase up-slope time such that microscopic contact areas are allowed to increase by plastic deformation, thereby avoiding a current density sufficiently high to cause expulsion. The second approach is to increase electrode force to create larger contact areas and thus reduce adversely-high current density on the microscopic level. The third approach is to decrease forge-delay time (apply forging-force early) to eliminate early expulsion. However, if the forging-force is applied too soon, a weak weld will be obtained due to lack of heat caused by the decreased contact resistance and increased heat dissipation. When an expulsion-free weld is obtained, an uninterrupted electrode expansion trace is obtained, as shown in Figure 39.

Parameter Development

Based on the above concepts, welding schedules for 0.063-inch thick bare 7075-T6 and 2024-T3 aluminum sheets were determined. At the beginning, welding without adhesive was conducted on spot-weld etched and FPL-etched surfaces. The joint strength and electrode indentation as a function of welding current for three welding schedules are shown in Figure 40 for 0.063-inch thick bare 7075-T6 sheets cleaned with a spot-weld etch. The longest welding time (20 cycles, Schedule I) produced highest electrode indentation with high scatter in joint strength. The 8-cycle welding time (Schedule III) gave the lowest electrode indentation and the lowest joint strength. Schedule II (12-cycle welding time) produced welds of relatively high strength from 670 lbs. to 1020 lbs. in the current range of 19.5 to 22.1 KA. This schedule also provided the best combination of high strength and minimum electrode indentation.

A forging-force was added to Schedule II and three forge-delay times were employed to investigate the effect of forge-delay time on joint strength. A long forge-delay time of 15 cycles not only produced a short weld-current range, but also caused expulsion at relatively low welding current. A 10-cycle forge-delay provided some improvement, but the welding current range was still only 1.8 KA. When the forge-delay time was reduced to 5 cycles, the welding current range increased by 3.1 KA from 20.7 KA to 23.8 KA. Therefore, welding Schedule II with forge-delay time of 5 cycles is recommended for welding of the spot-weld etched bare 7075-T6 aluminum sheet. The welding current ranges and the corresponding joint strengths for six welding schedules are listed in Table VII.

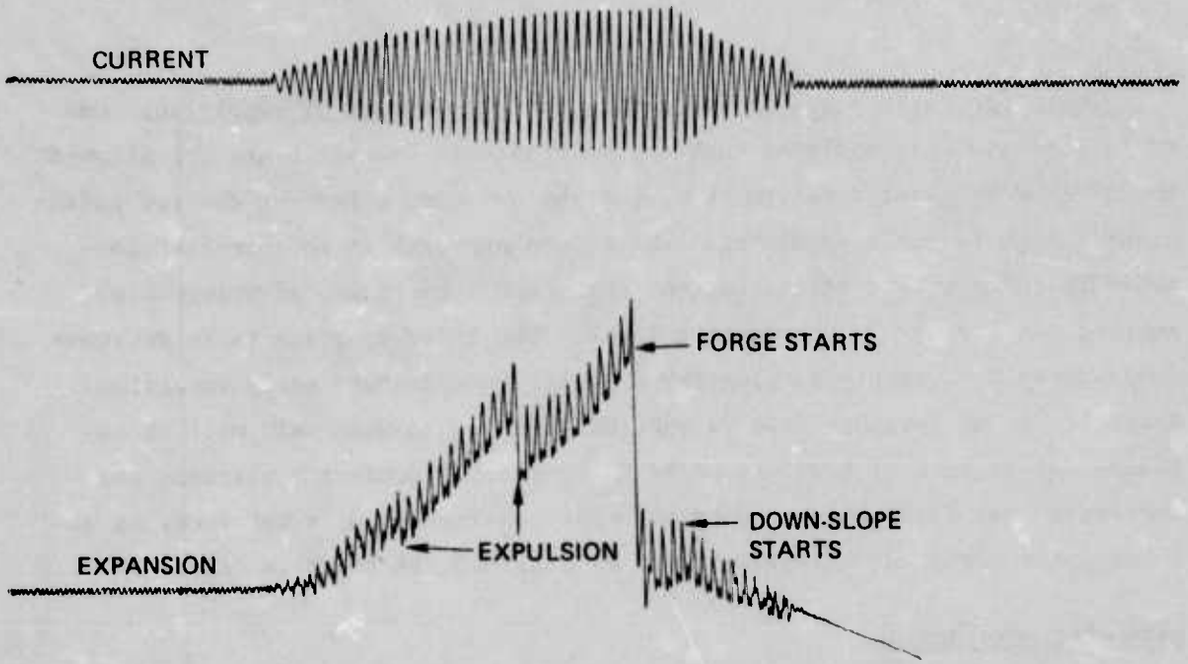


FIGURE 38. CURRENT AND NUGGET EXPANSION TRACES SHOWING EXPULSION

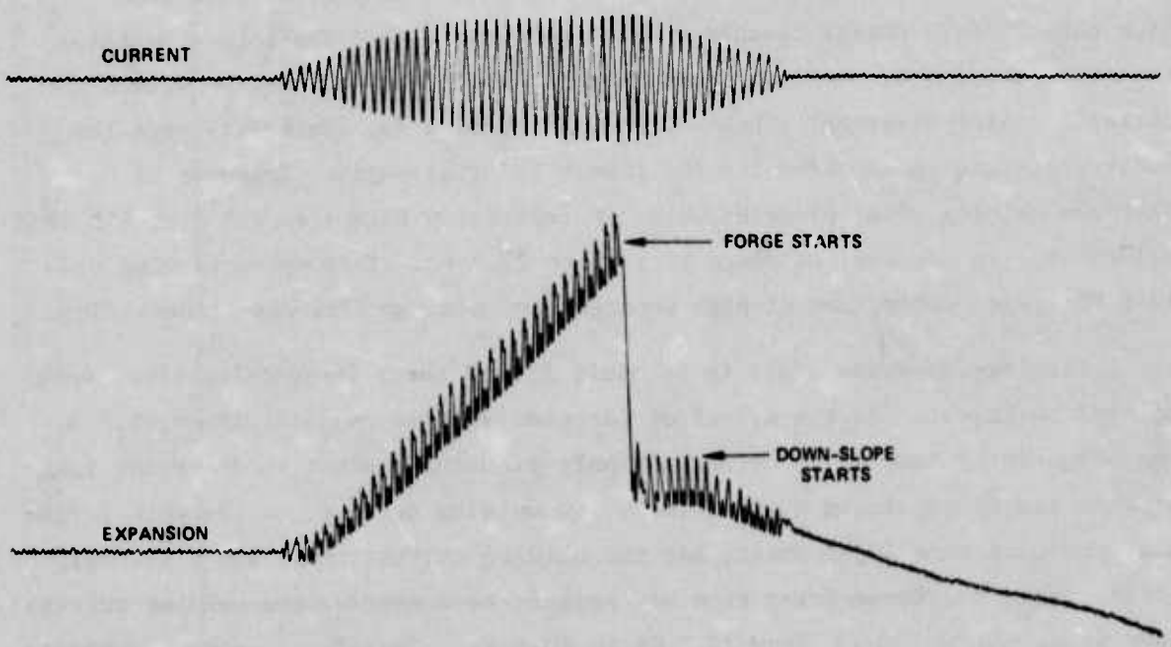


FIGURE 39. CURRENT AND NUGGET EXPANSION TRACES SHOWING NO EXPULSION

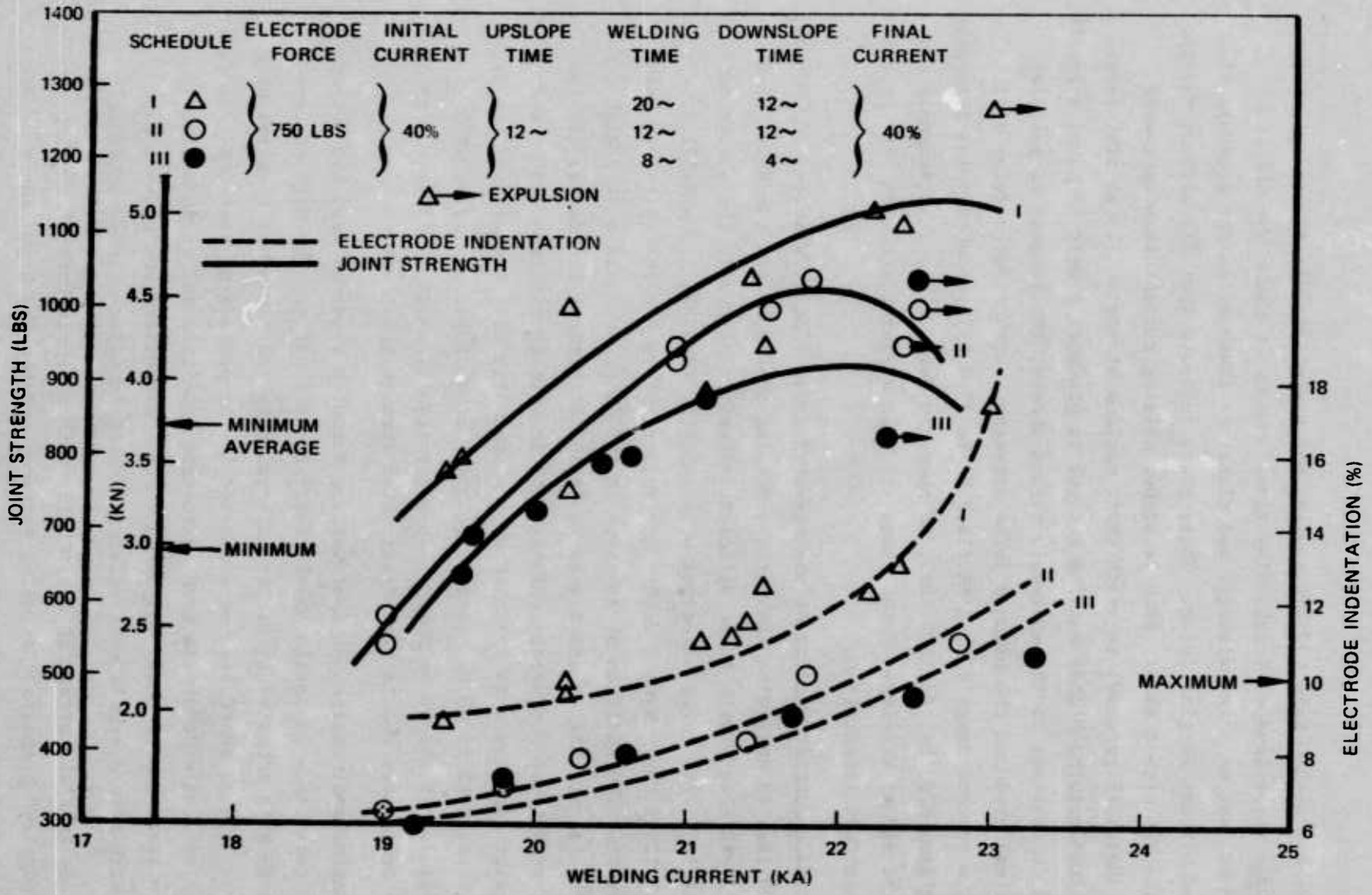


FIGURE 40. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION WITHOUT FORGING FORCE; BARE 7075-T6, SPOT-WELD ETCH

For FPL etched bare 7075-T6 sheets, the basic Schedule II was again used with three variations of forge-delay time. Figure 41 shows the effect of welding current on joint strength and electrode indentation for Schedule II with and without forging force. These plots indicate that (1) without forging force the FPL etched sheets require higher welding current than spot-weld etched sheets (Figure 40) to reach their maximum strength, (2) shorter forge-delay times require higher welding current to produce a weld of equal strength, and (3) in contrast to the spot-weld etched sheets, the longest forge-delay (15 cycles) produced the highest joint strength. With a forge-delay of 15 cycles, a current range of 4.2 KA (18.7 KA to 22.9 KA) produced joint strengths ranging from 670 lbs. to 1200 lbs., as shown in Table VIII. This schedule provided the widest welding-current range and highest joint strength with acceptable electrode indentation.

Surface contact resistance was measured under electrode forces of 750 lbs. and 1500 lbs. to determine the optimum welding schedules for the FPL-etched bare 7075-T6 sheets with three different adhesives placed in the joints before spot welding. The three adhesives were A-1396B, EA-9312, and ADX-373.1. Table IX lists the measured resistance values before the initiation of welding current. The addition of adhesive in the joint produces a very high contact resistance. The values listed in Table IX indicate two facts: (1) the contact resistance decreases somewhat with increasing electrode force and (2) contact resistance is affected by the viscosity of the adhesive (the viscosity of A-1396B is 20,000 centipoise and that of ADX-373.1 is 300,000 centipoise). It should be noted that the viscosity of an adhesive varies as welding progresses due to heat dissipation through the sheet.

Conventional resistance spot-welding normally requires very low surface contact resistance to obtain consistent joint strengths. The high contact resistance with adhesive is rather extraordinary and therefore requires unconventional welding schedules, as discussed in the proceeding sections. If an improper welding schedule is used, premature expulsion and an undersized nugget will be experienced. Figure 42 shows a nonuniform and undersized nugget with severe expulsion resulting from an improper welding schedule.

A low initial current in conjunction with a slower rate of up-slope heating "gradually" preheats the faying surface, reduces the high contact resistance, and uniformly expands the nugget. Thus on a microscopic scale, the

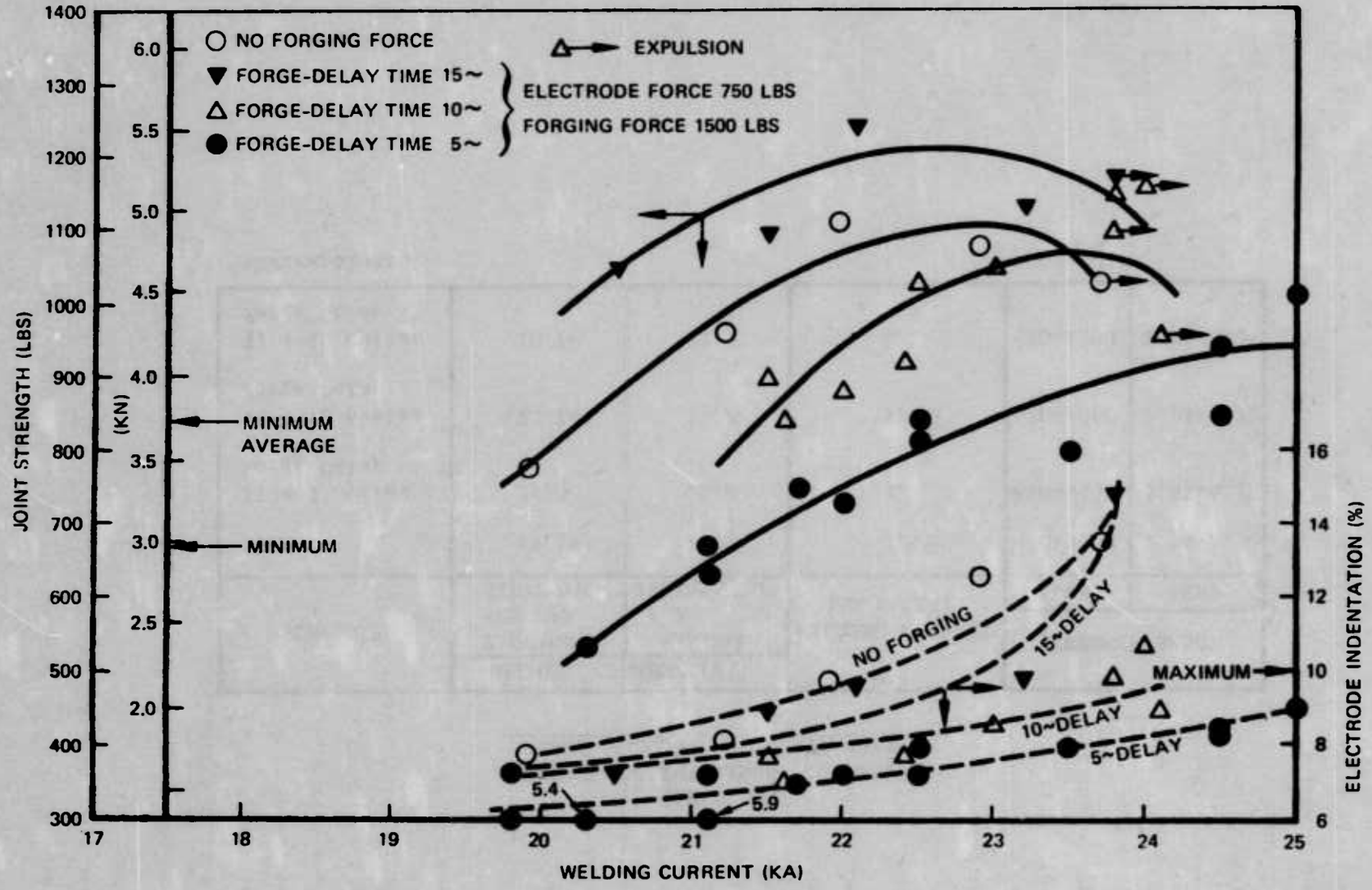


FIGURE 41. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION WITH AND WITHOUT FORGING FORCE; BARE 7075-T6, FPL ETCH

TABLE VIII
WELDING CURRENT RANGE FOR 7075-T6
BARE ALUMINUM USING FPL ETCH

SCHEDULE	WELDING CURRENT (KA)		WELDING CURRENT RANGE (KA)	STRENGTH RANGE	
	REQUIRED FOR MIN STRENGTH	MAXIMUM FOR 10% INDENTATION		(LBS)	(KN)
II	19.3*	22.2	2.9	670-1080	2.95-4.80
II + 5 cycles Forge Delay	21.3	25.0	3.7	670-940	2.95-4.18
II + 10 cycles Forge Delay	20.7*	23.8	3.1	670-1060	2.95-4.72
II + 15 cycles Forge Delay	18.7*	22.9	4.2	670-1200	2.95-5.34

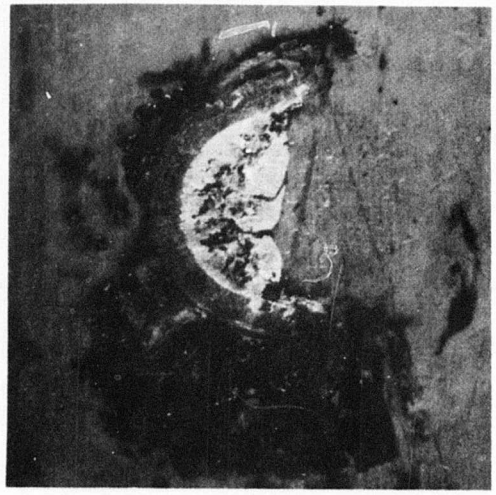
*Extrapolated

TABLE IX

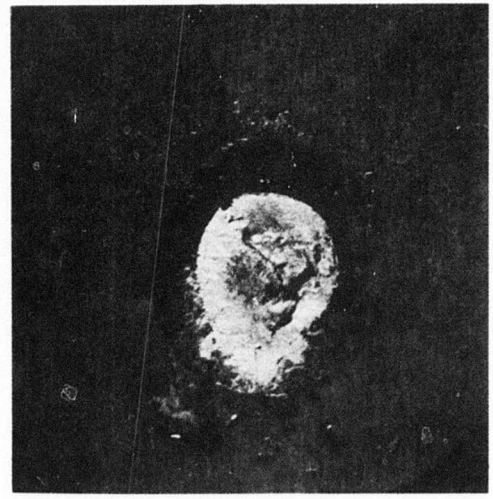
SURFACE CONTACT RESISTANCE UNDER VARIOUS CONDITIONS*

ELECTRODE FORCE		NO ADHESIVE		ADHESIVES		
LB	KN	SPOT-WELD ETCH	FPL ETCH	A-1396B	EA-9312	ADX-373.1
1700	7.50	10-66μohms	30-280μohms	2.7×10^{3}-10^{4} μohms	9×10^{3}- 10^{4} μohms	10^{4*} μohms
3400	15.00			2.0×10^{3}-6.5×10^{3} μohms	9×10^{3}-10^{4} μohms	10^{4*} μohms

*Much greater than 10^{4} μohms, beyond meter capacity



1.6 KN
(360 lb.)
Hysol 373



1.78 KN
(410 lb.)
B.F. Goodrich A1396B

FIGURE 42. DEFECTIVE SPOT WELDS RESULTING FROM INADEQUATE WELDING SCHEDULES

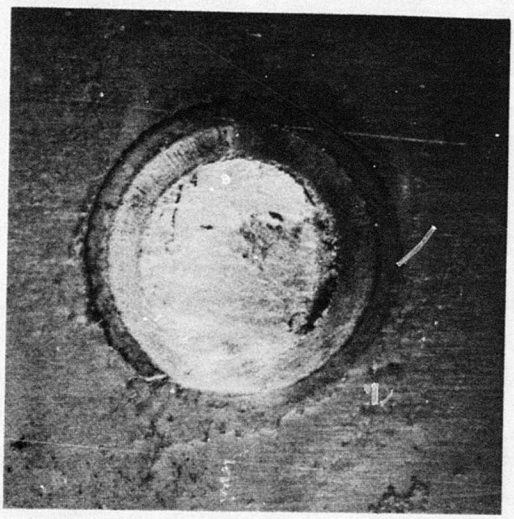
current density becomes more normal during welding and premature expulsion is avoided. Thus, a strong, expulsion-free, uniform nugget, as shown in Figure 43, can be obtained.

Welding parameters for deoxidized (for spot welding) and FPL etched surfaces on bare 7075-T6 and 2024-T3 of 0.063-inch thick sheets were determined. A-1396B and PE-130 adhesives were used. The contact resistance on deoxidized surfaces (spot-weld etch) without adhesive was under 30 μohms and on FPL etched surfaces was in the range of 25 to 150 μohms. To avoid expulsion, welding parameters were changed, as discussed in the preceding sections.

Figure 44 shows the strength-current curve for deoxidized bare 7075-T6 sheet using both adhesives and the welding schedule included in the figure. Expulsion was not observed throughout the current range. At a welding current of 22.5 KA, weld strength over 1000 lbs. can be obtained with electrode indentation of 8%. Without forging force, the weld strength was about 150 lbs. lower.

Bare 2024-T3 sheets using the same adhesives were welded through a range of current from 20.5 KA to 23.2 KA, as shown in Figure 45. Without forging force, the weld strength was again lower than that with forging force. Increasing electrode and forging force to 1200 and 3000 lbs., respectively, decreased weld strength drastically at lower current ranges. The other welding parameters are the same as those listed in Figure 44. The welding current range should be between 22.5 KA and 23.0 KA. Since the welding schedules for both 7075-T6 and 2024-T3 are essentially the same, the schedule for 7075-T6 was used to weld 2024-T3 sheets afterwards.

Welding schedules for FPL-etched bare 7075-T6 sheet with A-1396B are listed in Figure 46. In this investigation, three sets of electrode force and forging-force combinations were used. The effect of welding current on joint strength and electrode indentation is shown in the same figure. The 800-lb/2000-lb. force combination permitted a wider welding-current range than the other force-combinations. Furthermore, this force-combination also produced the highest joint strength among the three force-combinations investigated. The acceptable range in welding current was approximately 3.8 KA (from 19 KA to 22.8 KA).



4.67 KN
(1050 LB.)
B.F. GOODRICH A1396B

FIGURE 43. GOOD SPOT WELD PRODUCED BY PROPER WELDING SCHEDULE

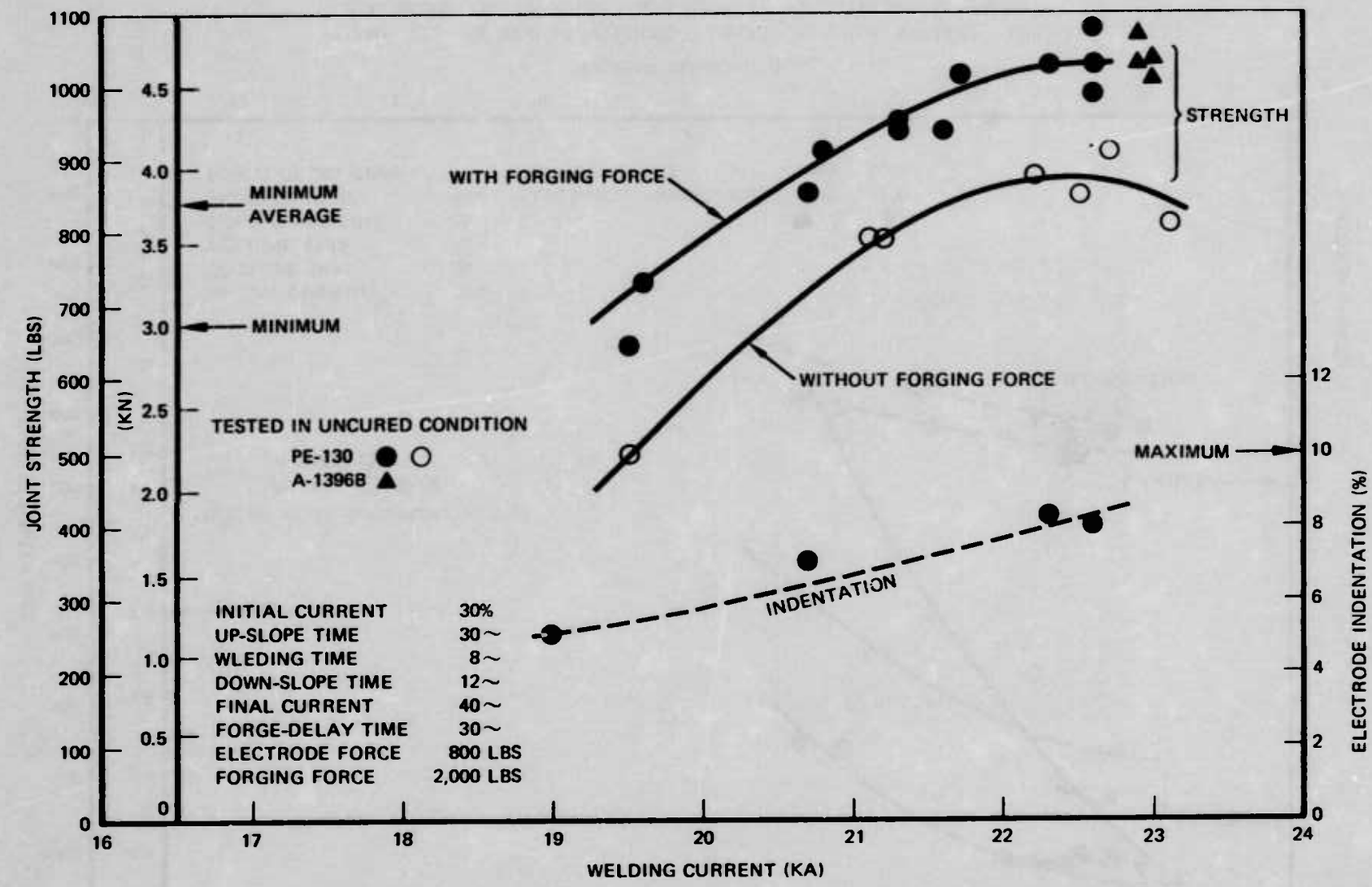


FIGURE 44. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION; BARE 7075-T6, DEOXIDIZED SURFACES

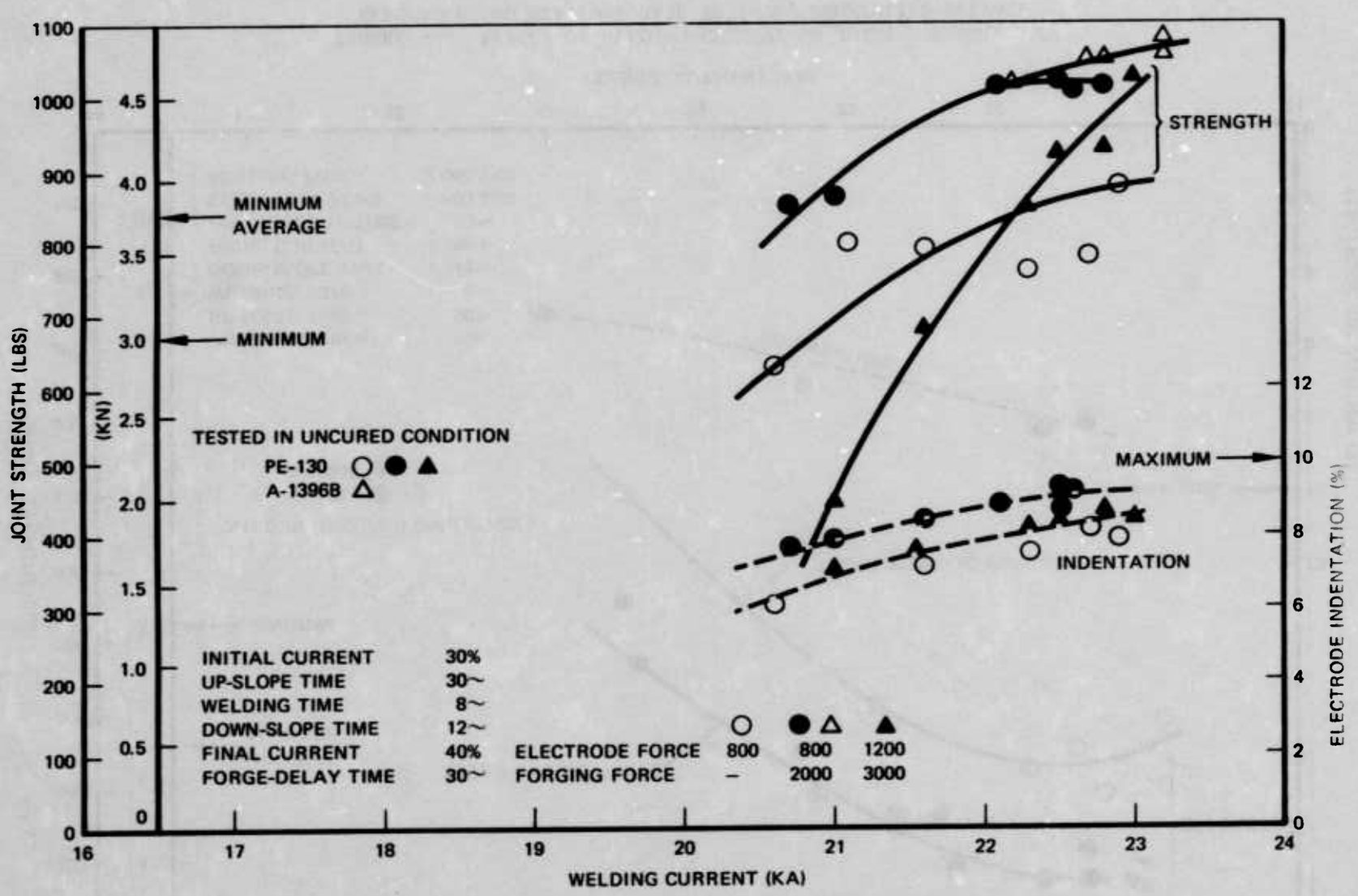


FIGURE 45. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION; BARE 2024-T3, DEOXIDIZED SURFACES

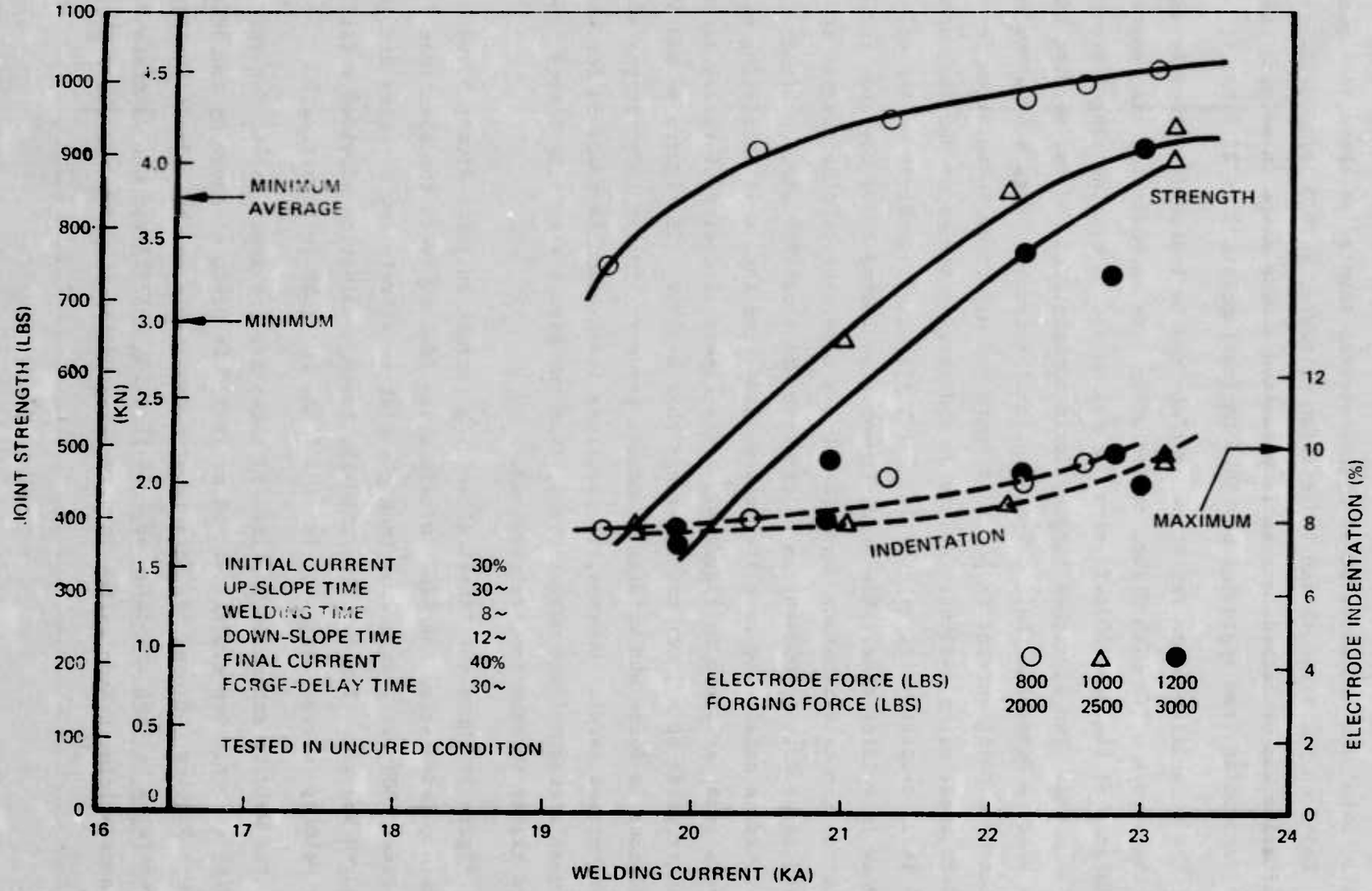


FIGURE 46. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION; BARE 7075-T6, FPL ETCH, A-1396B

When the FPL etch and PE-130 adhesive were used for bare 7075-T6 sheets, expulsion was observed at higher current levels, as shown in Figure 47. Based on the strength and indentation criteria, an 800-lb/2000-lb. force-combination was preferred because it permitted a wide range in welding current, extending from approximately 18.5 KA (extrapolated) to 22.5 KA.

The durability of an FPL etched surface may be improved further by sealing the porous oxide with dichromate solution (see Appendix 1). The contact resistance of the bare 2024-T3 aluminum sealed for 90 minutes ranges from 80 to 400 μohms. Two electrode forging force combinations and two welding times were used to determine their effects on joint strength. Figure 48 shows the effect of welding current on joint strength and electrode indentation for bare 2024-T3 sheet using A-1396B. Electrode and forging forces of 800 lbs. and 2000 lbs., respectively, gave higher joint strength regardless of the difference in welding time. Electrode indentation seemed to be the same for both electrode forces evaluated. When PE-130 was used, the welding current required to produce a 1000-lb. joint strength was about 800 amperes higher for the schedule consisting of a 16-cycle welding time than that consisting of an 8-cycle time, as shown in Figure 49. The higher viscosity of PE-130 allowed stronger welds at a lower current range than A-1396B. In Figures 48 and 49, variations in force and welding schedules produced similar indentations at a given current level. However, if electrode indentation is compared for welds of equal strength (same nugget size), then the higher electrode forces produced higher indentation, as expected.

Figure 50 shows the effect of welding current on joint strength and electrode indentation for bare 7075-T6 using PE-130. When the electrode force was under 1000 lbs., expulsion took place at relatively low currents and joint strength was low. The 1000-lb./2500-lb. force combination provided a fairly wide welding-current range (at least 2.5 KA) and good joint strength.

The welding schedules for 2024-T3 sheet are the same, except for the welding current when either A-1396B or PE-130 is used, as shown by comparison between Figures 48 and 49. This is also applicable to the 7075-T6 sheets. Therefore, a welding schedule for 7075-T6 using A-1396B was not determined. The same welding schedules for 7075-T6 using PE-130 should be adequate for A-1396B.

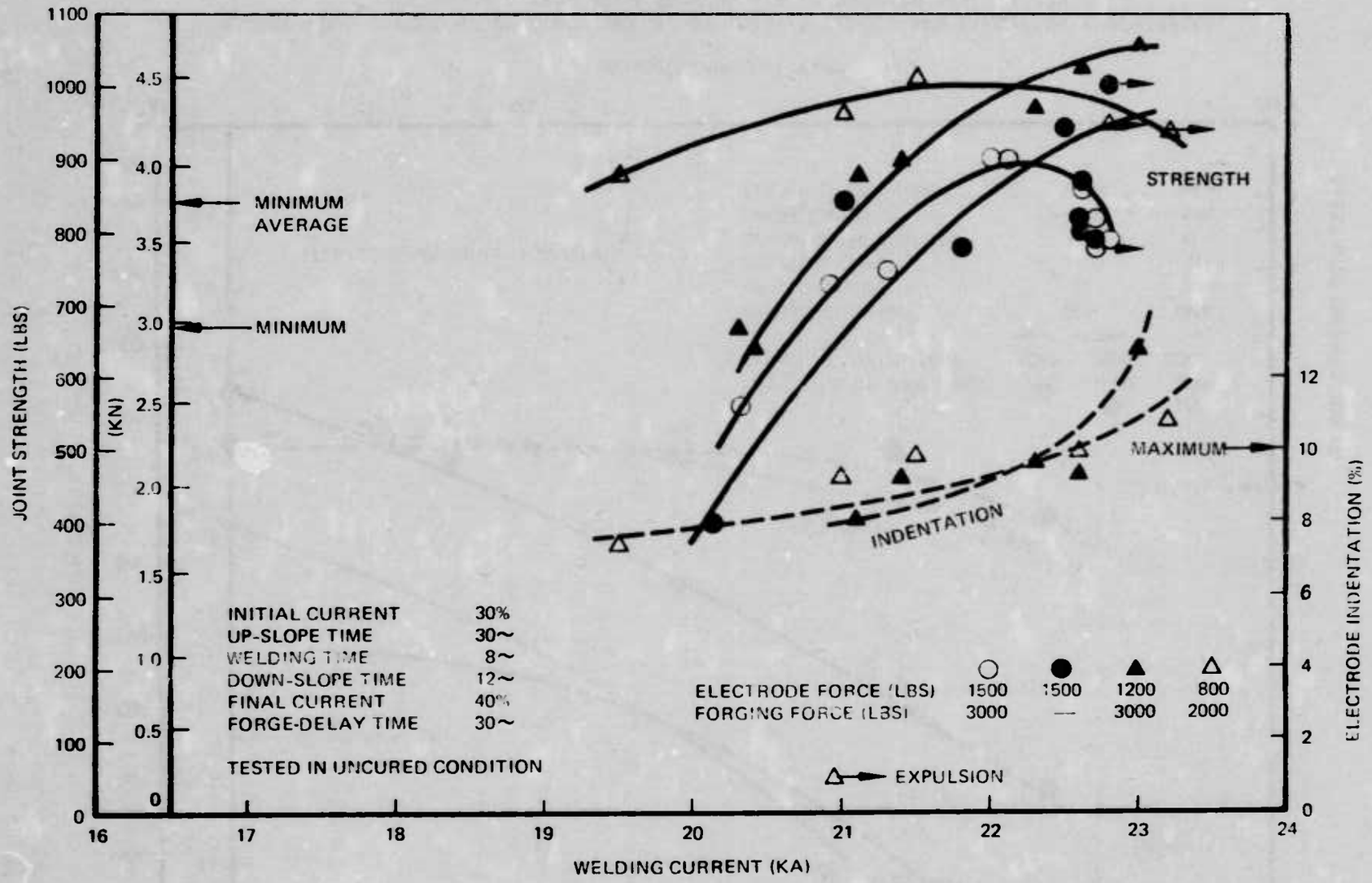


FIGURE 47. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION; BARE 7075-T6, FPL ETCH, PE-130

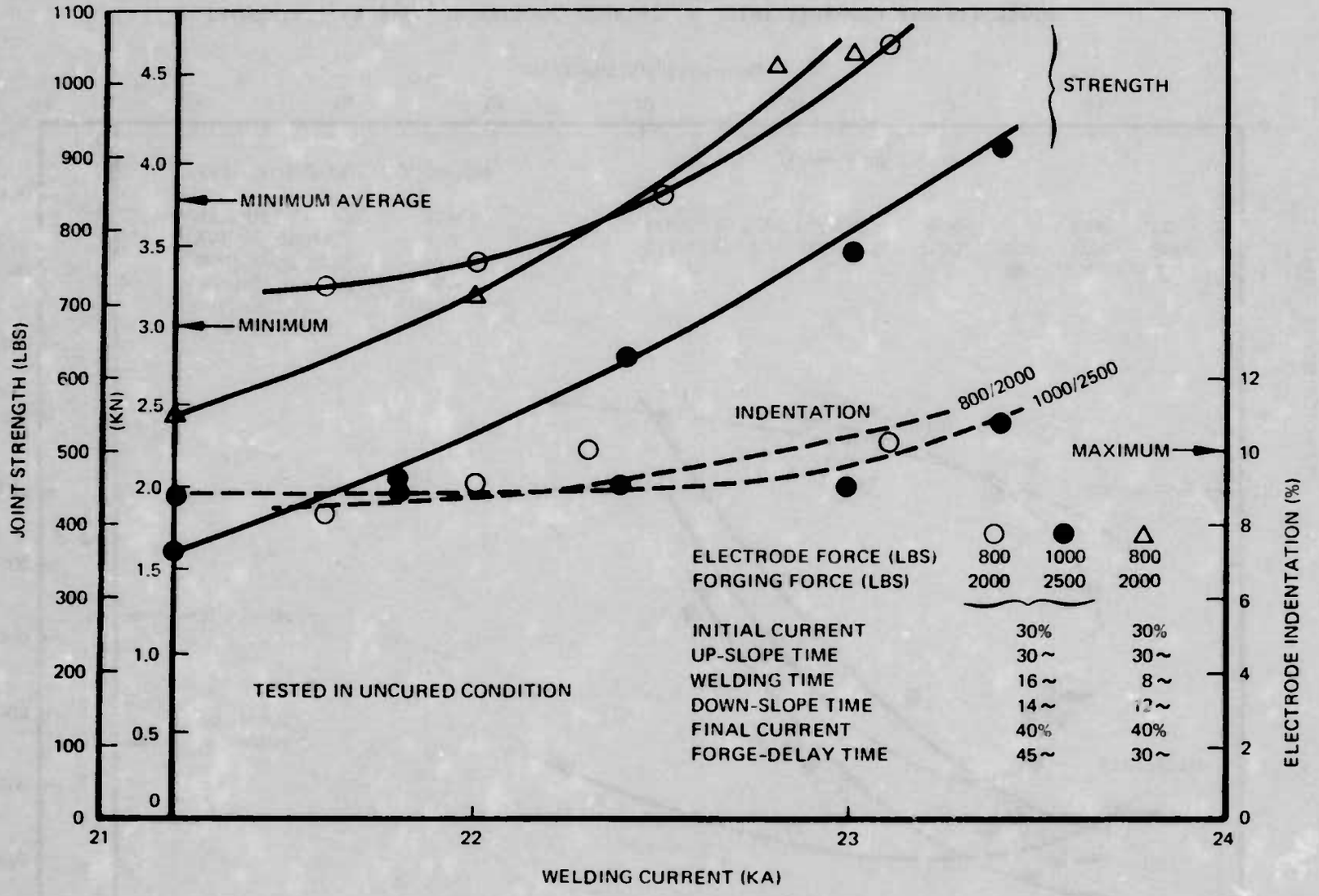


FIGURE 48. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION; BARE 2024-T3, FPL ETCH PLUS 90 MIN DICHROMATE SEAL, A-1396B

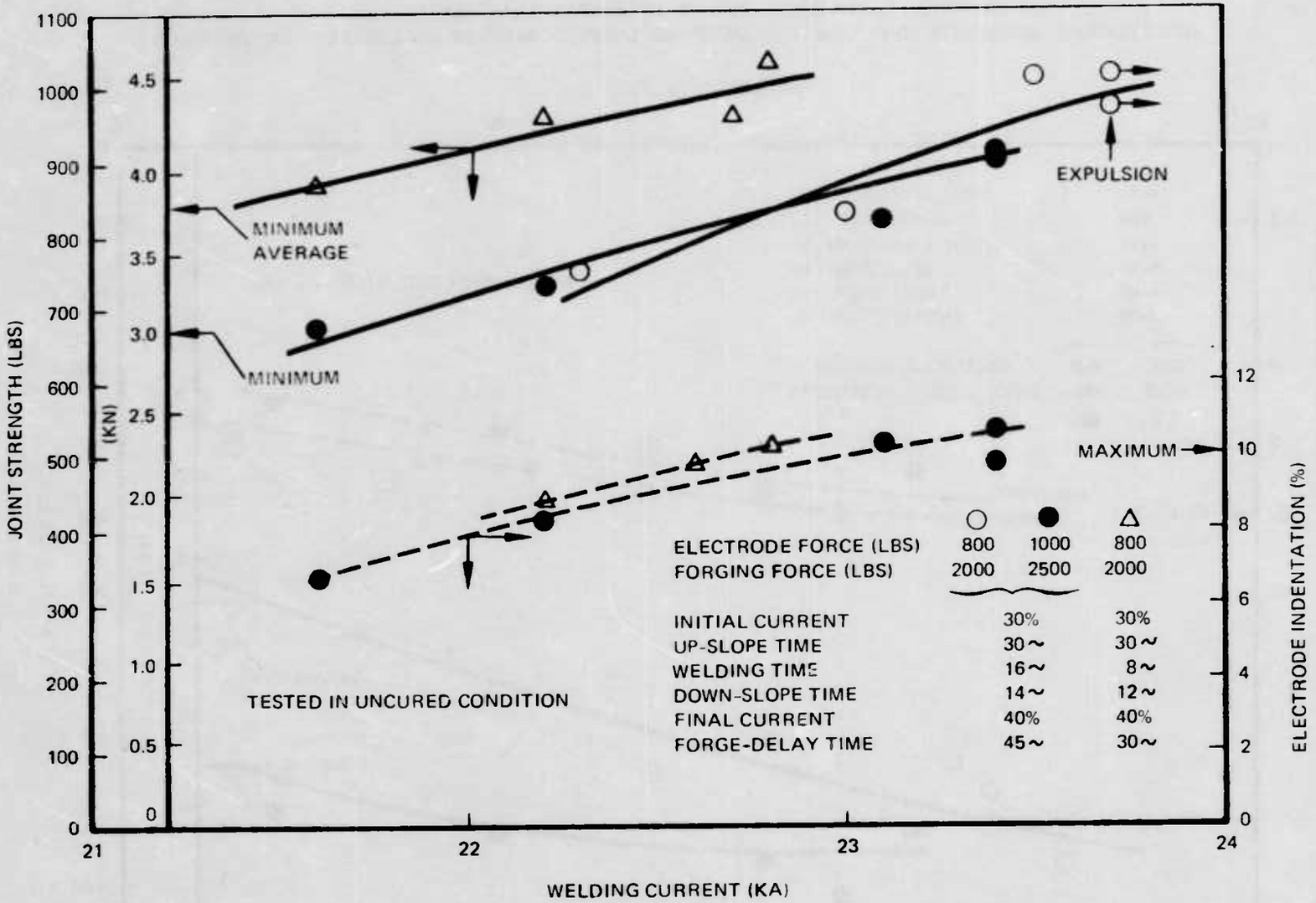


FIGURE 49. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION; BARE 2024-T3; FPL ETCH PLUS 90 MIN DICHROMATE SEAL, PE-130

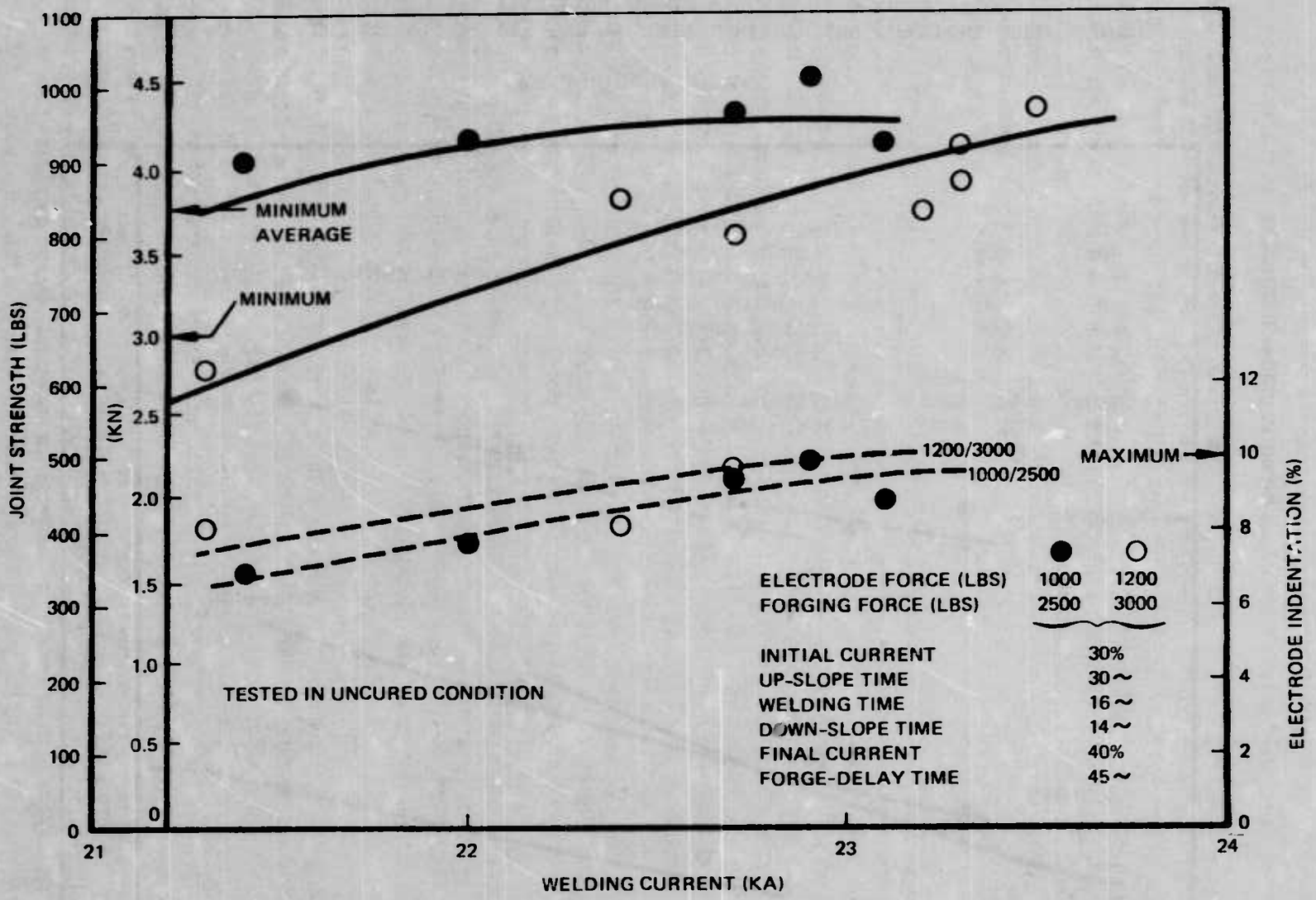


FIGURE 50. EFFECT OF WELDING CURRENT ON JOINT STRENGTH AND ELECTRODE INDENTATION; BARE 7075-T6, FPL ETCH PLUS 90 MIN DICHROMATE SEAL, PE-130

An analysis of Figures 40 and 41 and Figures 44 through 50 was made to specify recommended welding schedules for each system. The factors influencing the recommendations were based upon:

1. A spot-weld strength to equal or exceed values required by the MIL-W-6858 specification.

2. A maximum electrode indentation of 10%.

3. No expulsion.

4. The maximum latitude in welding current which will meet the requirements of (1), (2), and (3).

Based upon these considerations, the recommended welding parameters were established as listed in Table X.

The welding-current range for FPL-etched sheets is as wide as that for spot-weld etched sheets without adhesive. On the other hand, the dichromate seal did reduce the acceptable welding-current range from 3.5 KA to 2.0 KA, which still provides good latitude.

Welding of ammonium tartrate, sulfuric acid, and phosphoric-acid anodized surfaces of bare 7075 aluminum was investigated. Referring to Table VI, the difficulties of welding these surfaces were anticipated because of high contact resistance. Sheets anodized at 10V for 10 minutes in ammonium tartrate exhibited a contact resistance ranging from 90 μohms to 300 μohms. Using PE-130 and welding schedules for FPL-etched surfaces, expulsion took place at a welding current as low as 18.8 KA. The nugget expansion trace recorded on the oscillograph indicated that expulsion occurred between the 8th and 12th cycle of the welding time. Forge-delay times, shorter than 8 cycles, prevented expulsion but caused formation of small weld nuggets of low strength. Consequently, higher electrode force and forging force were in order. When the electrode and forging forces were increased to 1500 lbs. and 3000 lbs., respectively (other parameters remaining the same), expulsion was still observed with a weld strength of 1040 lbs. Further increases in electrode and forging forces were beneficial for elimination of expulsion, but they increased electrode indentation beyond acceptable levels. Therefore, the surface anodized

TABLE X
WELDING SCHEDULES FOR ALUMINUM ALLOYS
(0.063-INCH OR 1.6 mm) WITH OR WITHOUT ADHESIVE

PARAMETERS	7075-T6 SPOT WELD ETCH	7075-T6 FPL ETCH	7075-T6 or 2024-T3	2024-T3	7075-T6
			FPL ETCH	FPL ETCH PLUS 90-MIN. DICHROMATE SEAL	
	w/o ADHESIVE	w/o ADHESIVE	A-1396B PE-130	A-1396B PE-130	PE-130
Electrode Material Electrode Diameter in.	CLASS I 5/8				
Electrode Dome Radius, in.	4	4	6	6	6
Electrode Force lbs.	750	750	800	800	1000
Forge Force lbs.	1500	1500	2000	2000	2500
Forge Delay Time, Cycle	5	15	30	30	45
Initial Current %	40	40	30	30	30
Up-Slope Time, Cycle	12	12	30	30	30
Welding Time, Cycle	12	12	8	8	16
Down-Slope Time, Cycle	12	12	12	12	14
Final Current,%	40	40	40	40	40
Welding Current Range, KA	10.7-23.8	19*-23.0	19.0*-22.5	(1) 21.8*-23.0	21.0*-23.0
Max.Joint Stg.,lbs	1170	1200	1000	1000	800

*Extrapolated values

at 10V in ammonium tartrate solution was considered to be unweldable under the conditions evaluated.

Bare 7075-T6 of 0.063-inch thick anodized in ammonium tartrate solution at 5V for 5 minutes (80-230 μohms) exhibited good weldability with PE-130. Expulsion was not observed under the welding schedule for FPL-etched sheet. Sulphuric acid and phosphoric-acid anodized (200-500 μohms) surfaces gave severe expulsion problems as suspected. Since the durability of the surfaces treated with FPL etch plus dichromate seal is excellent[3], further welding studies on anodized surfaces were terminated.

The contact resistance for various surface treatments were overlapping with a maximum value of 500 μohms produced by the low-voltage anodizing treatments. Yet, the weldability of these surfaces varied tremendously. By adding adhesives, the contact resistance increased to several thousand microhms, as shown in Table IX, but weldability was not influenced greatly by the presence of the adhesive. These facts lead one to believe that contact resistance alone does not dictate the weldability of the oxide surface. Chemical composition, crystal structure, and physical and mechanical properties of these oxides probably have much to do with weldability just as with durability. It is theorized that the thickness and crystal structure of the oxide layer are the major constraints to be considered as affecting welding parameters.

To fabricate peel test specimens, 0.020-inch thick bare 7075-T6 and 2024-T3 sheet were used and welding schedules for de-oxidized, FPL-etched, FPL-etched plus 90 minutes dichromate sealed surfaces using Goodrich A1396B and 0500 PE-130 adhesives were determined. These welding schedules are listed in Table XI. Because of the extremely thin sheets, the temperature gradient during welding was relatively high. This high temperature gradient and high contact resistance in the joint, particularly in the FPL-etch plus 90 minutes dichromate sealed surfaces, produced a very narrow welding current range. Therefore, occasionally expulsion occurred in the FPL-etch and 0500 PE 130 adhesive joints and more often in the FPL-etch plus 90 minutes dichromate sealed surfaces and both adhesives. Referring to Table XI, it can be noted that the electrode force required to produce a better weld is higher for sheets having higher contact resistance. These schedules are not optimum. The only requirement was that it produced a minimum joint strength of 140 lbs. and the minimum average of 175 lbs. specified in the MIL-W-6858. However, in some specimens, the joint strength exceeded 200 lbs. (See Appendix II).

TABLE XI
WELDING SCHEDULES FOR 0.020-IN.
BARE 7075-T6 AND 2024-T3

	7075-T6						2024-T3					
	A-1396B			0500 PE-130			A-1396B			0500 PE-130		
	Deoxi-dize	FPL	FPL + 90-Min.	Deoxi-dize	FPL	FPL + 90-Min.	Deoxi-dize	FPL	FPL + 90-Min.	Deoxi-dize	FPL	FPL + 90-Min.
Electrode Force (lbs)	400	400	500	400	500	500	400	450	550	400	450	550
Forge Force (lbs)	1100	1100	1100	1100	1250	1100	1100	1150	1100	1100	1150	1100
Initial Current (%)	30	30	30	30	30	30	30	30	30	30	30	30
Up-Slope Time (Cycles)	16	20	16	20	26	16	8	20	16	12	20	16
Welding Time (Cycles)	0	0	0	0	0	0	4	0	0	0	0	0
Down-Slope Time (Cycles)	4	4	4	4	4	4	4	4	4	4	4	4
Final Current (%)	40	40	40	40	40	40	40	40	40	40	40	40
Forge Delay Time (Cycles)	10	16	16	16	18	16	10	16	16	10	16	16
Welding Current (KA)	20.2	21.8	23.6	21.5	24.2	23.3	20.2	22.5	23.6	21.1	22.8	23.6

As a result of this study, it may be concluded that:

1. High resistance surfaces for weldbonding can be spot-welded by using appropriate welding schedules either on single-phase or three-phase frequency-converter type spot-welding machine to produce Class A welds per MIL-W-6858 specification.

2. With weldbonding surfaces of high resistance, controlled up-slope heating and proper forging force and forge-delay time are required to eliminate expulsion.

3. Surfaces anodized in the low-voltage sulfuric acid and phosphoric acid solutions were unweldable under the conditions evaluated.

4. Electrode movement can be used to detect precise time of occurrence and degree of expulsion.

5. Surface contact resistance is not the only factor which affects weldability. Physical and mechanical properties of the oxide probably have some influence on weldability also.

PHASE III - CHARACTERIZATION STUDIES

This phase of the program was designed to evaluate the results of Phases I and II with particular emphasis on determining the effects of the surface treatment and the adhesive modification on initial static strengths, standard environmental exposure, and stressed environmental exposure. Standard lap shear tests, wedge tests, peel tests, and stress-corrosion tests were conducted. Bond strengths have been determined under various conditions of temperature and environmental exposure to establish baseline values for each adhesive system or surface preparation. These permit direct comparison of the effects of each adhesive modification and surface preparation under the same environmental conditions. The results of tests conducted are included in Tables XII through XX.

Analysis of the data obtained to date indicates the following:

1. The Goodrich A-1396B adhesive system has proved to be a good choice as a spot-weld bonding adhesive giving reasonable ease of weld-through capability coupled with excellent strengths over the temperature range of -67F to 180F. Most of the strength levels reported are comparable to those obtained with standard structural films in use in the industry. The adhesive also exhibits good resistance to the standard environmental exposures on both 7075-T6 and 2024-T3 alloys. Problem areas to be evaluated more fully are in the sensitivity of the adhesive to glueline thickness control as noted in some of the individual test results, the increased brittleness of the chromate modification as noted in the initial crack growth of the wedge test results, and the decreased lap shear strength of the spot-weld bonded 2024-T3 specimens as compared to the 7075-T6 specimens which may be related to the lower yield strength of the 2024-T3 alloy.

2. The wedge test specimen appears to provide an excellent, economical, and rapid comparison of the environmental resistance of the surface treatment and the adhesive system as long as caution is exercised in comparing variations within the test rather than from test to test. Variables of adhesive and glueline thickness must be considered when comparing wedge test results from test to test and mode of failure must be used for comparison.

3. Analysis of the environmental test results in Tables XVI, XVII, XIX and XX indicates the following:

   a. The overall average strength retention in unstressed exposure calculated including alloy type, exposure type and adhesive shows the weldbonded specimens retaining 73.5%, 93.3% and 94.3% of the control value for deoxidized, FPL etched, and FPL etch/90-minute sealed treatments respectively. Similarly, the adhesive bonded specimens showed a retention of 70.8%, 86.5%, and 87.8% of control for deoxidized, FPL etched, and FPL etch/90-minute sealed surfaces respectively. These values show a significant improvement is attained in going from a bayerite oxide layer (deoxidize treatment) to a boehmite oxide layer (FPL etch and FPL/90) in the unstressed exposure. However, only a very slight improvement is gained by thickening of the oxide layer by dichromate sealing.

   b. By using the same analysis procedure to compare overall strength retention versus adhesive type and/or alloy type, it can be shown that the PE-130 provides a slight decrease in retention overall, and that the 2024-T3 alloy is significantly lower in overall retention than the 7075-T6 alloy.

   c. Certain anomalies are found in Tables XVI and XVII where strength levels after exposure for the FPL/90 surfaces are significantly lower than for the FPL etch surfaces and in some cases are even lower than the deoxidized surfaces. Examination of the failed specimens shows only a clean adhesive failure with no visual evidence of bondline corrosion at the interface. Failure of these surfaces is presently being attributed to possible variations in processing causing either variations in thickness or porosity of the oxide layer.

   d. The data in Tables XIX and XX cannot be treated quantitatively at this time due to a combination of variables within the test matrix. For example, the use of the percentage of initial static strength introduces a large variation in the load level as applied to the aluminum substrate which in turn causes differing rates of corrosion. In addition, there are subtle variations in processing which could not be defined which add variations in the time to

failure. Certain trends are apparent in the data in that the FPL etched specimens have significantly improved corrosion resistance over the deoxidized surface and the PE-130 appears to show an additional improvement. No significant improvements over the FPL etch by dichromate sealing can be determined at this time. Additional data will be obtained to clarify these conclusions.

4. The data received so far has confirmed the original hypothesis and the overall direction of this program; namely, that the surface chemistry plays the predominant role in determining the resistance of a structural bond to a stressed environment. Standard spot-weld etch treatments produce a weak and porous layer of bayerite which will not maintain a structural bond for sufficient time. The use of the FPL etch produces a layer of boehmite on the surface which does provide a significant improvement in bond durability. The use of anodize treatments can produce thicker, more adherent, and less porous films of boehmite which continue to show improvements in bond durability.

5. The effect of the increases of boehmite layer thickness on the weldability is a proportional increase in welding difficulty. This condition was discussed in more detail under welding developments with a comparison of the welding parameters with surface treatments. By proper adherence to welding theory, Class A spot welds can be made through durable surfaces.

6. The addition of small amounts of strontium chromate to the adhesive provides a significant improvement to the stress-environment durability of the bond as evidenced by the wedge test results. The chromate works in conjunction with the improved surface treatment to enhance the durability of the bond.

TABLE XII

COMPARISON OF ADHESIVE BOND LAP SHEAR(1) STRENGTHS VERSUS TEMPERATURES WITH SELECTED SURFACE TREATMENTS

ALLOY	SURFACE TREATMENT(2)	TEST TEMP.	ADHESIVE SYSTEM	
			A-1396B	PE-130
7075-T6	Deoxidize	-67F	4720	3800
		R.T.	4390	5320
		180F	2060	2710
	FPL Etch	-67F	5710	5110
		R.T.	5640	6210
		180F	2570	3520
	FPL Etch Plus 90-Min. Dichromate Seal	-67F	5560	6100
		R.T.	5360	5680
		180F	2560	3760
	Ammonium Tartrate Anodize	-67F	5940	3680
		R.T.	5230	5710
		180F	2440	3260
	Phosphoric Acid Anodize	-67F	6100	4370
		R.T.	6140	6330
		180F	4330	3980
2024-T3	Deoxidize	-67F	4350	4670
		R.T.	5340	4700
		180F	3300	2850
	FPL Etch	-67F	5470	5010
		R.T.	5490	6650
		180F	3290	3200
	FPL Etch Plus 90-Min. Dichromate Seal	-67F	4820	4630
		R.T.	5620	6400
		180F	2830	3370

(1) See Appendix 3 for Specimen Configuration
(2) See Appendix 1 for Treatment Details

TABLE XIII

COMPARISON OF SPOT-WELD BOND LAP SHEAR STRENGTHS(1) VERSUS TEMPERATURES AFTER SELECTED SURFACE TREATMENTS

ALLOY	SURFACE TREATMENT(2)	TEST TEMP.	ADHESIVE SYSTEM	
			A-1396B	PE-130
7075-T6	Deoxidize	-67F	3360	2850
		R.T.	4310	4190
		180F	3120	3280
	FPL Etch	-67F	4730	2880
		R.T.	4870	4790
		180F	3330	3100
	FPL Etch Plus 90-Min. Dichromate Seal	-67F	4400	3880
		R.T.	4460	4790
		180F	3250	3100
2024-T3	Deoxidize	-67F	2860	2640
		R.T.	3400	3440
		180F	2490	2840
	FPL Etch	-67F	3590	3290
		R.T.	3740	3760
		180F	2740	2890
	FPL Etch Plus 90-Min. Dichromate Seal	-67F	3290	3460
		R.T.	3510	3710
		180F	2820	2500

(1) See Appendix 3 for Specimen Configuration
(2) See Appendix 1 for Treatment Details

TABLE XIV

INITIAL WEDGE TEST EVALUATION[1]
2024-T3 AND 7075-T6
SELECTED CORROSION RESISTANT SYSTEMS
SALT SPRAY EXPOSURE*

ALLOY	TREATMENT	ADHESIVE	INITIAL CRACK LENGTH (L_0)	Δ CRACK LENGTH-1HR. (L_1)	Δ CRACK LENGTH-4HR. (L_2)	Δ CRACK LENGTH-21HR. (L_3)	TOTAL CRACK GROWTH ($L_1+L_2+L_3$)
2024-T3	Deoxidize	A-1396B	1.95"	2.05"	0.29"	0.42"	2.76"
2024-T3	Deoxidize	PE-130	2.44"	0.72"	0.00"	0.07"	0.79"
7075-T6	Deoxidize	A-1396B	2.08"	1.87"	0.10"	0.08"	2.05"
7075-T6	Deoxidize	PE-130	2.58"	0.60"	0.04"	0.13"	0.77"
2024-T3	FPL Etch	A-1396B	1.96"	1.02"	0.02"	0.01"	1.05"
2024-T3	FPL Etch	PE-130	2.48"	0.00"	0.04"	0.00"	0.04"
7075-T6	FPL Etch	A-1396B	1.98"	0.08"	0.07"	0.10"	0.25"
7075-T6	FPL Etch	PE-130	2.53"	0.00"	0.00"	0.02"	0.02"
2024-T3	FPL + 90-Min. Seal	A-1396B	2.14"	1.02"	0.02"	0.01"	1.05"
2024-T3	FPL + 90-Min. Seal	PE-130	2.48"	0.00"	0.04"	0.00"	0.04"
7075-T6	FPL + 90-Min. Seal	A-1396B	2.18"	0.53"	0.09"	0.00"	0.62"
7075-T6	FPL + 90-Min. Seal	PE-130	2.77"	0.00"	0.00"	0.00"	0.00"
7075-T6	Phosphoric Anodize	A-1396B	2.03"	0.00"	0.00"	0.04"	0.04"
7075-T6	Phosphoric Anodize	PE-130	2.21"	0.00"	0.00"	0.00"	0.00"

* Exposed at a temperature of 95F to a fine mist of 5% sodium chloride solution.

(1) See Appendix 3 for Specimen Configuration

TABLE XV
INITIAL WEDGE TEST EVALUATION(1)
2024-T3 AND 7075-T6
SELECTED CORROSION RESISTANT SYSTEMS
HUMIDITY EXPOSURE*

ALLOY	TREATMENT	ADHESIVE	INITIAL CRACK LENGTH (L_0)	Δ CRACK LENGTH-1HR. (L_1)	Δ CRACK LENGTH-4HR. (L_2)	Δ CRACK LENGTH-21HR. (L_3)	TOTAL CRACK GROWTH ($L_1+L_2+L_3$)
2024-T3	Deoxidize	A-1396B	2.03"	1.73"	0.16"	0.00"	1.89"
2024-T3	Deoxidize	PE-130	2.51"	0.09"	0.09"	0.00"	0.18"
7075-T6	Deoxidize	A-1396B	2.03"	1.92"	0.00"	0.03"	1.95"
7075-T6	Deoxidize	PE-130	2.88"	0.07"	0.00"	0.00"	0.07"
2024-T3	FPL Etch	A-1396B	2.01"	0.64"	0.21"	0.05"	0.90"
2024-T3	FPL Etch	PE-130	2.38"	0.07"	0.00"	0.02"	0.09"
7075-T6	FPL Etch	A-1396B	2.02"	0.00"	0.07"	0.12"	0.19"
7075-T6	FPL Etch	PE-130	2.62"	0.00"	0.00"	0.00"	0.00"
2024-T3	FPL + 90-Min. Seal	A-1396B	2.47"	0.69"	0.00"	0.00"	0.69"
2024-T3	FPL + 90-Min. Seal	PE-130	2.47"	0.00"	0.00"	0.00"	0.00"
7075-T6	FPL + 90-Min. Seal	A-1396B	2.20"	0.04"	0.10"	0.00"	0.14"
7075-T6	FPL + 90-Min. Seal	PE-130	2.42"	0.00"	0.00"	0.00"	0.00"

* Exposed at a temperature of 120F and 95% relative humidity.
(1) See Appendix 3 for Specimen Configuration

TABLE XVI
COMPARISON OF STRENGTHS AFTER VARIOUS ENVIRONMENTAL
EXPOSURES — STANDARD ½" OVERLAP SHEAR(1)

ALLOY	ADHESIVE	TREATMENT	CONTROL STRENGTH (PSI)	ENVIRONMENTAL EXPOSURE			
				60 DAY SALT SPRAY (PSI/% CONT)	60 DAY HUMIDITY (PSI/% CONT)	3.5% SALT WATER IMMERSION (PSI/% CONT)	30 DAY THERMAL CYCLE(2) (PSI/% CONT)
7075-T6	A-1396B	Deoxidize	4390	2270/52	2280/52	4100/93	4440/101
		FPL Etch	5640	4950/88	4320/77	5430/96	6200/110
		FPL Etch Plus 90-Min. Dichromate Seal	5360	4720/88	3740/70	4410/82	5590/104
7075-T6	PE-130	Deoxidize	5320	3610/68	2630/49	4580/86	4580/86
		FPL Etch	6210	6200/100	5450/88	7060/114	5860/94
		FPL Etch Plus 90-Min. Dichromate Seal	5680	6440/113	5220/92	6870/121	6460/114
2024-T3	A-1396B	Deoxidize	5340	3600/67	3090/58	3960/74	3500/66
		FPL Etch	5490	4670/85	4560/83	4770/87	4790/87
		FPL Etch Plus 90-Min. Dichromate Seal	5620	3640/65	2860/51	4750/85	4670/83
2024-T3	PE-130	Deoxidize	4700	3410/73	2290/49	3960/84	3440/73
		FPL Etch	6650	4700/71	3480/52	4840/73	5040/76
		FPL Etch Plus 90-Min. Dichromate Seal	6400	5330/83	4720/74	6430/100	5040/79

(1) See Appendix 3 for Specimen Configuration
(2) 1 hr. @ 180F plus
1 hr. @ -67F plus
22 hr. @ 120F @ 95% R.H.

TABLE XVII
COMPARISON OF STRENGTHS AFTER VARIOUS ENVIRONMENTAL
EXPOSURES — STANDARD 1" WELDBOND OVERLAP SHEAR(1)

ALLOY	ADHESIVE	TREATMENT	CONTROL STRENGTH (PSI)	ENVIRONMENTAL EXPOSURE			
				60 DAY SALT SPRAY (PSI/% CONT)	60 DAY HUMIDITY (PSI/% CONT)	3.5% SALT WATER IMMERSION (PSI/% CONT)	30 DAY THERMAL CYCLE(2) (PSI/% CONT)
7075-T6	A-1396B	Deoxidize	4310	3730/87	3420/79	4300/100	3700/86
		FPL Etch	4870	4570/94	4620/95	4850/100	4930/101
		FPL Etch Plus 90-Min. Dichromate Seal	4460	3760/84	3920/88	4840/109	4640/104
7075-T6	PE-130	Deoxidize	4190	3080/74	2220/53	4020/96	2840/68
		FPL Etch	4790	4550/95	4490/94	4880/102	4380/91
		FPL Etch Plus 90-Min. Dichromate Seal	4790	4520/94	4230/88	4800/100	4430/92
2024-T3	A-1396B	Deoxidize	3400	1890/56	2560/75	3000/88	2870/84
		FPL Etch	3740	3550/95	3530/94	3560/95	3650/98
		FPL Etch Plus 90-Min. Dichromate Seal	3510	3060/87	3420/97	3420/97	3360/96
2024-T3	PE-130	Deoxidize	3440	1200/35	1940/56	2800/81	2040/59
		FPL Etch	3760	2730/73	2930/78	3570/95	3450/92
		FPL Etch Plus 90-Min. Dichromate Seal	3710	3250/88	3290/89	3740/101	3420/92

(1) See Appendix 3 for Specimen Configuration
(2) 1 hr. @ 180F plus
1 hr. @ -67F plus
22 hr. @ 120F @ 95% R.H.

TABLE XVIII

T-PEEL[1] STRENGTHS — ROOM TEMPERATURE

ALLOY	TREATMENT	ADHESIVE	PEEL (LBS/IN.)
2024-T3	Deoxidize	A-1396B	15.5
		PE-130	18.0
	FPL Etch	A-1396B	29.0
		PE-130	22.0
	FPL Etch/90-Min.Dichromate Seal	A-1396B	19.0
		PE-130	24.4
7075-T6	Deoxidize	A-1396B	13.8
		PE-130	14.8
	FPL Etch	A-1396B	13.7
		PE-130	12.0
	FPL Etch/90-Min.Dichromate Seal	A-1396B	9.0
		PE-130	--

(1) See Appendix 3 for Specimen Configuration

TABLE XIX

STRESS CORROSION DATA — ADHESIVE BONDED JOINTS[2]
SALT SPRAY EXPOSURE

ALLOY	TREATMENT	ADHESIVE	LOAD LEVEL (% OF ISS*/PSI)	AVG TIME[1] TO FAIL (HRS)
7075-T6	Deoxidize	A-1396B	80/2950	16
			60/2000	20
			40/1470	----
		PE-130	80/3800	18
			60/2560	70
			40/1920	----
	FPL Etch	A-1396B	80/4920	74
			60/2820	500
			40/2030	800
		PE-130	80/4920	100
			60/3840	730
			40/2500	1144
	FPL Etch/90-Min. Dichromate Seal	A-1396B	80/3400	67
			60/2860	480
			40/2000	----
		PE-130	80/5060	12
			60/3470	180
			40/2390	----
2024-T3	Deoxidize	A-1396B	80/3000	20
			60/3060	16
			40/1500	16
		PE-130	80/4120	12
			60/3060	16
			40/2000	310
	FPL Etch	A-1396B	80/3540	70
			60/2650	188
			40/1760	475**
		PE-130	80/5180	14
			60/3960	40
			40/2620	230
	FPL Etch/90-Min. Dichromate Seal	A-1396B	80/3720	86
			60/2640	144
			40/----	----
		PE-130	80/5480	16
			60/3840	160
			40/----	----

(1) Average of 3 Specimens Each
(2) See Appendix 3 for Specimen Configuration
* Initial Static Strength
** First Failure of the Group

TABLE XX

STRESS CORROSION DATA — SPOT-WELD JOINTS (1)
SALT SPRAY EXPOSURE

ALLOY	TREATMENT	ADHESIVE	LOAD LEVEL (% OF ISS*/PSI	AVERAGE (2) TIME TO FAILURE (HRS)
2024-T3	Deoxidize	A-1396B	80/2070	50
			60/1660	210
			40/----	----
		PE-130	80/3000	18
			60/2210	45
			40/1395	324
	FPL Etch	A-1396B	80/2800	154
			60/2145	288
			40/1550	
		PE-130	80/2960	360
			60/2210	700
			40/1515	

(1) See Appendix 3 for Specimen Configuration
(2) Average of 3 Specimens Each

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

The objectives of this program were to develop a spot-weld bonding system for aluminum that would produce Class A welds and have the strength and environmental durability of the state-of-the-art adhesive systems. These have been met with a surface treatment consisting of the FPL etch followed by a 90-minute seal in boiling water/sodium dichromate solution and an adhesive formulation containing A-1396B modified with 3% strontium chromate. This combination provides a system which is weldable (Class A welds), has good adhesion, and resists stressed environmental conditioning as well as state-of-the-art structural adhesive systems.

However, the surface treatment process developed is not optimum for two reasons. First, the basic FPL etch treatment is not completely reproducible except under carefully controlled conditions, thereby introducing some degree of error in the oxide layer thickness which then affects the weldability of the adherend. Second, the 90-minute seal process imposes a cost restriction on the manufacturing procedure both in time consumed in processing and in maintaining a large bath at temperatures of 208F-212F.

In addition, the basic strength properties of the adhesive have been altered slightly by the addition of the chromate filler, primarily the peel strength. Also, the present A-1396B system represents a service temperature use area of -67F to 180F which is somewhat restrictive for high performance aircraft.

Based on these conclusions, it is recommended that the surface treatment process be optimized based on the requirement of a tightly adherent oxide layer of boehmite ($\alpha Al_2O_3 \cdot H_2O$) to a controllable thickness of 400Å-700Å. One recommended procedure for accomplishment of this objective is a modification of the phosphoric acid anodize process which has been shown to provide a fairly thin oxide layer ($\approx$2000Å) with excellent adhesion and good bondline durability. It is also recommended that the adhesive formulation be optimized to provide maximum durability consistent with a minimum degradation of mechanical properties and that weldbonding adhesives capable of operating over a wider temperature range be evaluated and modified in a similar manner.

REFERENCES

1. Bowen, B. B., Herfert, R. E., and Wu, K. C., "Development of Corrosion Resistance Surface Treatments for Aluminum Alloys for Spot-Weld Bonding," Interim Technical Report No. 1, NOR 74-93, May 1974.

2. Bowen, B. B., Herfert, R. E., and Wu, K. C., "Development of Corrosion Resistance Surface Treatment for Aluminum Alloys for Spot-Weld Bonding," Interim Technical Report No. 2, NOR 74-231, August 1974.

3. Bowen, B. B., Herfert, R. E., and Wu, K. C., "Development of Corrosion Resistance Surface Treatment for Aluminum Alloys for Spot-Weld Bonding," Interim Technical Report No. 3, NOR 74-314, November 1974.

4. Wu, K. C., Northrop in-house research program, un-published data.

APPENDIX I

SURFACE PREPARATION DETAILS

SULPHURIC ACID ANODIZE

1. Degrease - Trichlorethane Vapor

2. Alkaline Clean - 10 to 15 min.
   Turco 4215-S - 6-8 oz./gal.
   Operate @ 155F $\pm$ 10°F

3. Deoxidize - 5-10 min.
   Amchem 7 - 2.7 to 3.3 oz./gal.
   Nitric Acid - 8 to 16% by volume
   Operate @ R.T.

4. Anodize 20 min. @ 10-17 VDC and 15-18 amp./ft.^{2} current density
   Sulphuric Acid - 15-18% by weight
   Operate @ Sp. Gravity 1.30 at R.T.

5. Neutralize
   Sodium Bicarbonate - 5-7% by weight
   Operate @ R.T.

6. Dichromate Seal - 15 min.
   Sodium Dichromate - 5 to 6.5% by weight
   Operate @ 208F to 212F

Note: De-ionized water used in mixing solutions and rinsing between operations.

FPL ETCH

1. Degrease - Trichlorethane Vapor

2. Alkaline Clean - 10 to 15 min.
   Turco 4215-S - 6-8 oz./gal.
   Operate @ 155F $\pm$ 10°F

3. Sulphuric Dichromate Etch - 10 min. $\pm$ 1 min.
   Sulphuric Acid - 38.5 to 41.5 oz./gal.
   Sodium Dichromate - 4.1 to 4.9 oz./gal.
   Operate @ 145F to 160F

Note: De-ionized water used in mixing solutions and rinsing between operations.

DEOXIDIZE

1. Degrease - Trichlorethane Vapor

2. Alkaline Clean - 10 to 15 min.
   Turco 4215-S - 6-8 oz./gal.
   Operate @ 155F $\pm$ 10°F

3. Deoxidize - 5-10 min.
   Amchem 7 - 2.7 to 3.3 oz./gal.
   Nitric Acid - 8% to 16% by volume
   Operate @ R.T.

Note: De-ionized water used in mixing solutions and rinsing between operations.

CHROMIC ACID ANODIZE

1. Degrease - Trichlorethane vapor

2. Alkaline Clean - 10-15 min.
   Turco 4215-S - 6-8 oz./gal.
   Operate @ 155F $\pm$ 10°F

3. Deoxidize - 5-10 min.
   Amchem 7 - 2.7 to 3.3 oz./gal.
   Nitric Acid - 8% to 16% by volume
   Operate @ R.T.

4. Anodize (see below)
   Chromic Acid - 6.7 to 13.4 oz./gal.
   Operate @ 104F $\pm$ 4°F

   Anodize for 40 min. while regulating the voltage as follows:

   a. Gradually increase the voltage for the first 10 minutes from 0 to 40 in steps of not more than 5 volts.

   b. For the next 20 minutes hold @ 40 volts.

   c. Increase gradually to 50 volts within 5 minutes and hold for 5 minutes.

   Note: The current density at the higher voltage should be 2.5 amps/ft.^{2} of anode surface.

5. Dichromate Seal - 15 min.
   Sodium Dichromate - 5 to 6.5% by weight
   Operate @ 208F to 212F

Note: De-ionized water used in mixing solutions and rinsing between operations.

ALODINE 1200 PROCESS

1. Degrease - Trichlorethane Vapor

2. Alkaline Clean - 10 to 15 min.
   Turco 4215-S - 6-8 oz./gal.
   Operate @ 155F ± 10°F

3. Deoxidize - 5 to 10 min.
   Amchem 7 - 2.7 to 3.3 oz./gal.
   Nitric Acid - 8 to 16% by volume
   Operate @ R.T.

4. Alodine 1200 - 1 to 3 min.
   Alodine 1200 power - 1 to 3 oz./gal.
   Mix thoroughly
   Maintain pH 1.5 to 2.0, adjust with Nitric Acid
   Operate @ 70F to 100F

Note: De-ionized water used in mixing solutions and rinsing between operations.

O-1 SPOT-WELD ACID ETCH FOR BARE ALUMINUM ALLOYS

1. Degrease - Trichlorethane Vapor

2. Alkaline Clean - 10 to 15 min.
   Turce 4215-S - 6-8 oz./gal.
   Operate @ 155F ± 10°F

3. Spot-Weld Acid Etch - 10 min. ± 1 min.
   Sulphuric Acid - 9 to 12 oz./gal.
   Sodium Dichromate - 5.3 to 7.4 oz./gal.
   Ammonium Bifluoride - 0.14 to 0.28 oz./gal.
   Operate @ R.T.

4. Alkaline Etch - 5 to 10 min.
   Sodium Hydroxide - 3.5 oz./gal.
   Sodium Gluconate - 0.035 oz./gal.
   Operate @ R.T.

5. Spot-Weld Acid Etch
   See #3 above

Note: De-ionized water used in mixing solutions and rinsing between operations.

O-8 SPOT-WELD ACID ETCH FOR CLAD ALUMINUM ALLOYS

1. Degrease - Trichlorethane Vapor

2. Alkaline Clean - 10-15 min.
   Turco 4215-S - 6-8 oz./gal.
   Operate at 155F $\pm$ 10°F

3. Spot-Weld Acid Etch - 10 to 20 min.
   Sulphuric Acid - 9 to 12 oz./gal.
   Sodium Dichromate - 5.3 to 7.4 oz./gal.
   Ammonium Bifluoride - 0.14 to 0.28 oz./gal.
   Operate @ R.T.

Note: De-ionized water used in mixing solutions and rinsing between operations.

PHOSPHORIC ACID ANODIZE

1. Degrease - Trichlorethane Vapor

2. Alkaline Clean - 10 to 15 min.
   Turco 4215-S - 6-8 oz./gal.
   Operate @ 155F ± 10°F

3. Deoxidize - 5-10 min.
   Amchem 7 - 2.7 to 3.3 oz./gal.
   Nitric Acid - 8 to 16% by volume
   Operate @ R.T.

4. Anodize 20-25 min. @ 10 ±1 VDC
   Phosphoric Acid - 11-16 oz. (vol. gal.
   Operate @ R.T.°

5. Oven dry at 150F-160F.

Note: De-ionized water used in mixing solutions and rinsing between operations.

APPENDIX II

MINIMUM REQUIRED SHEAR STRENGTH FOR SPOT WELD SHEAR SPECIMENS AND MINIMUM AVERAGE STRENGTH (ALUMINUM ALLOYS)

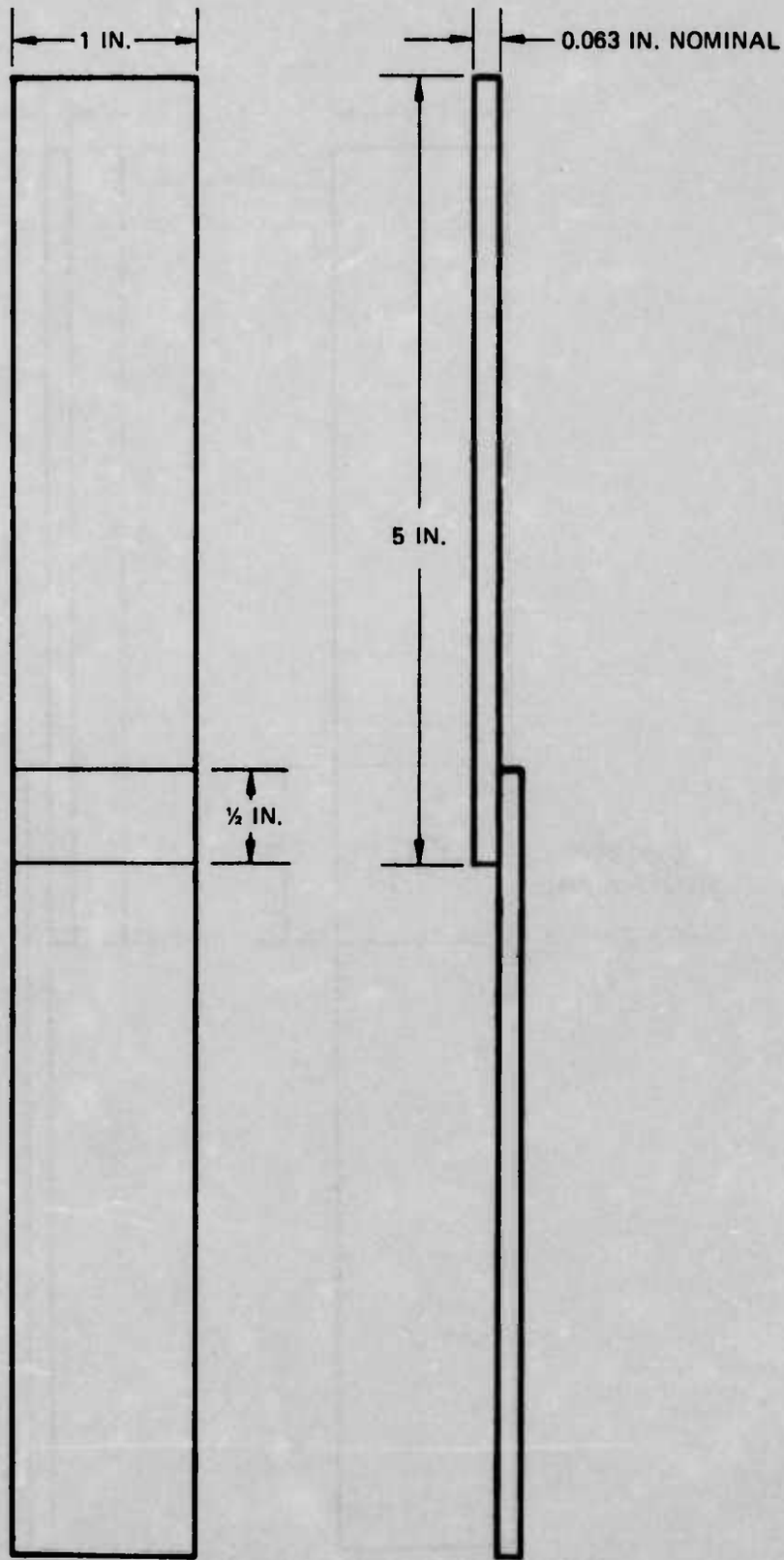
APPENDIX II

MINIMUM REQUIRED SHEAR STRENGTH FOR SPOT WELD SHEAR SPECIMENS
AND MINIMUM AVERAGE STRENGTH (ALUMINUM ALLOYS)

NOMINAL THICKNESS OF THINNER SHEET (INCH)	ULTIMATE STRENGTH 50,000+ PSI		ULTIMATE STRENGTH 35,000-55,000PSI		ULTIMATE STRENGTH 19,000-35,000PSI		ULTIMATE STRENGTH -19,500 PSI	
THICKNESS See Std M833528	POUNDS PER WELD							
	MIN	MIN AVG	MIN	MIN AVG	MIN	MIN AVG	MIN	MIN AVG
0.020	140	175	135	170	100	125	80	100
0.040	345	435	310	390	300	375	225	285
0.063	670	840	610	765	570	715	395	495
0.090	1255	1570	1000	1250	810	1090	595	745
0.125	2120	2650	1625	2035	1050	1315	785	985

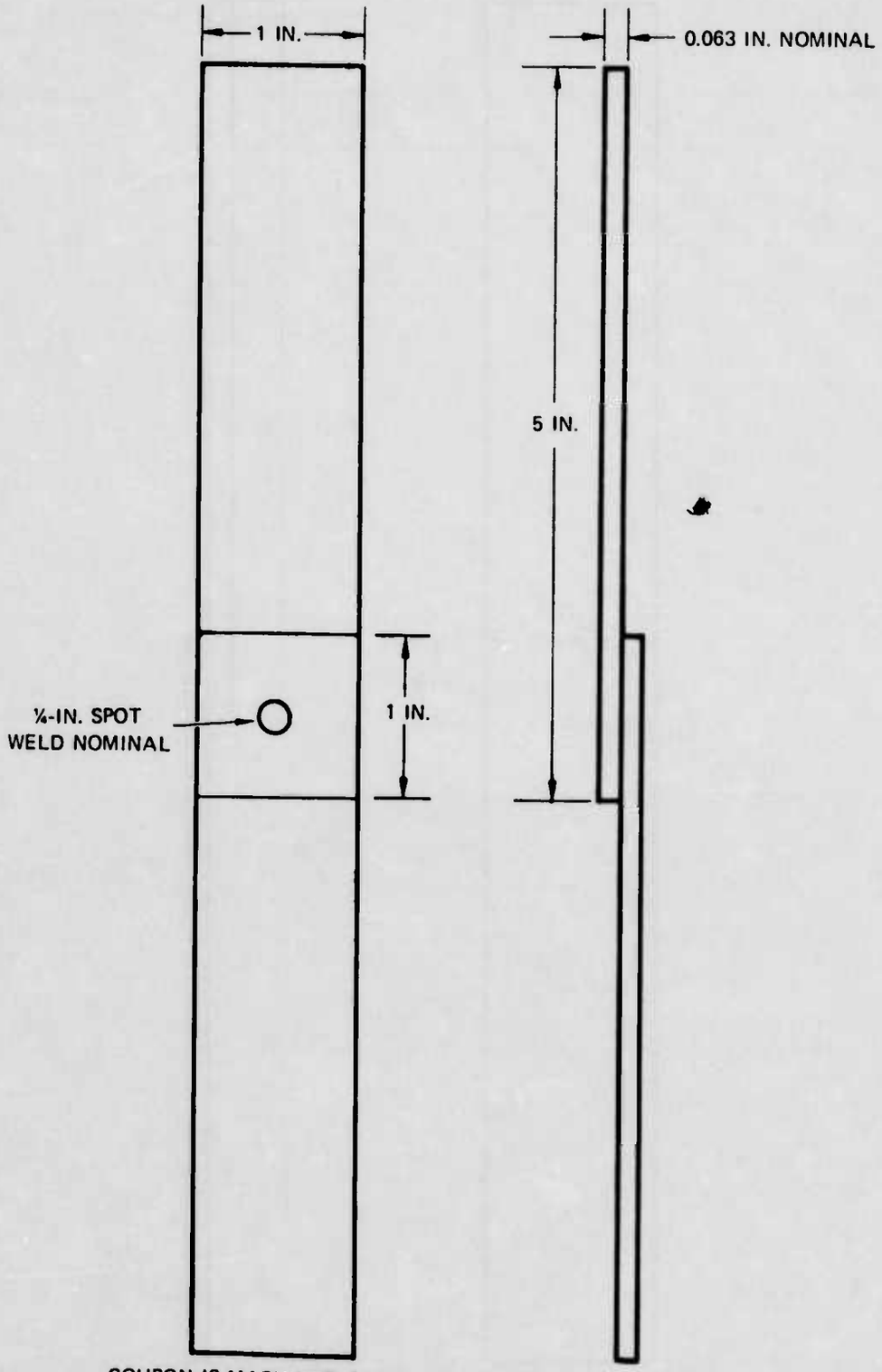
APPENDIX III

TEST SPECIMEN CONFIGURATIONS



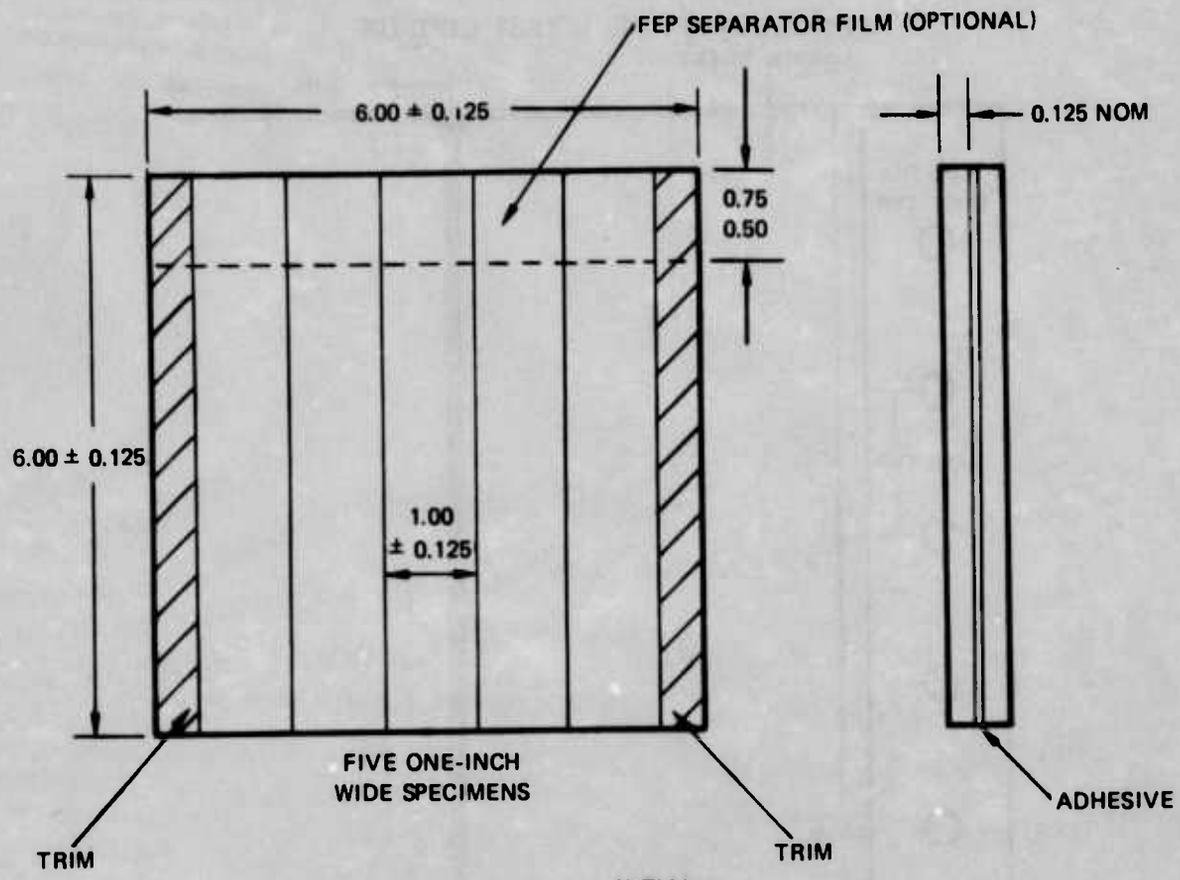
COUPON IS MACHINED FROM A 6-IN. WIDE BONDED PANEL

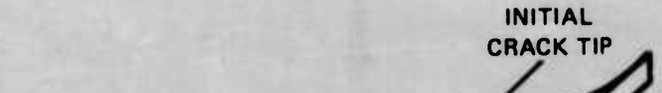
STANDARD ADHESIVE BOND LAP SHEAR COUPON



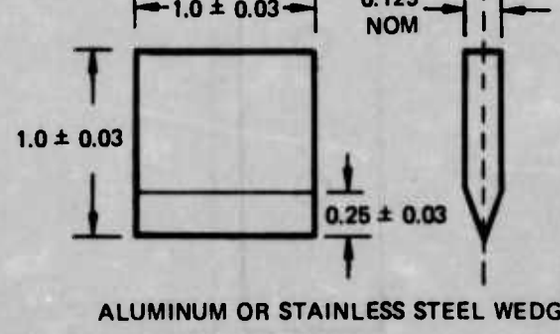
COUPON IS MACHINED FROM A 6-IN. WIDE BONDED PANEL

STANDARD WELD-BOND LAP SHEAR COUPON



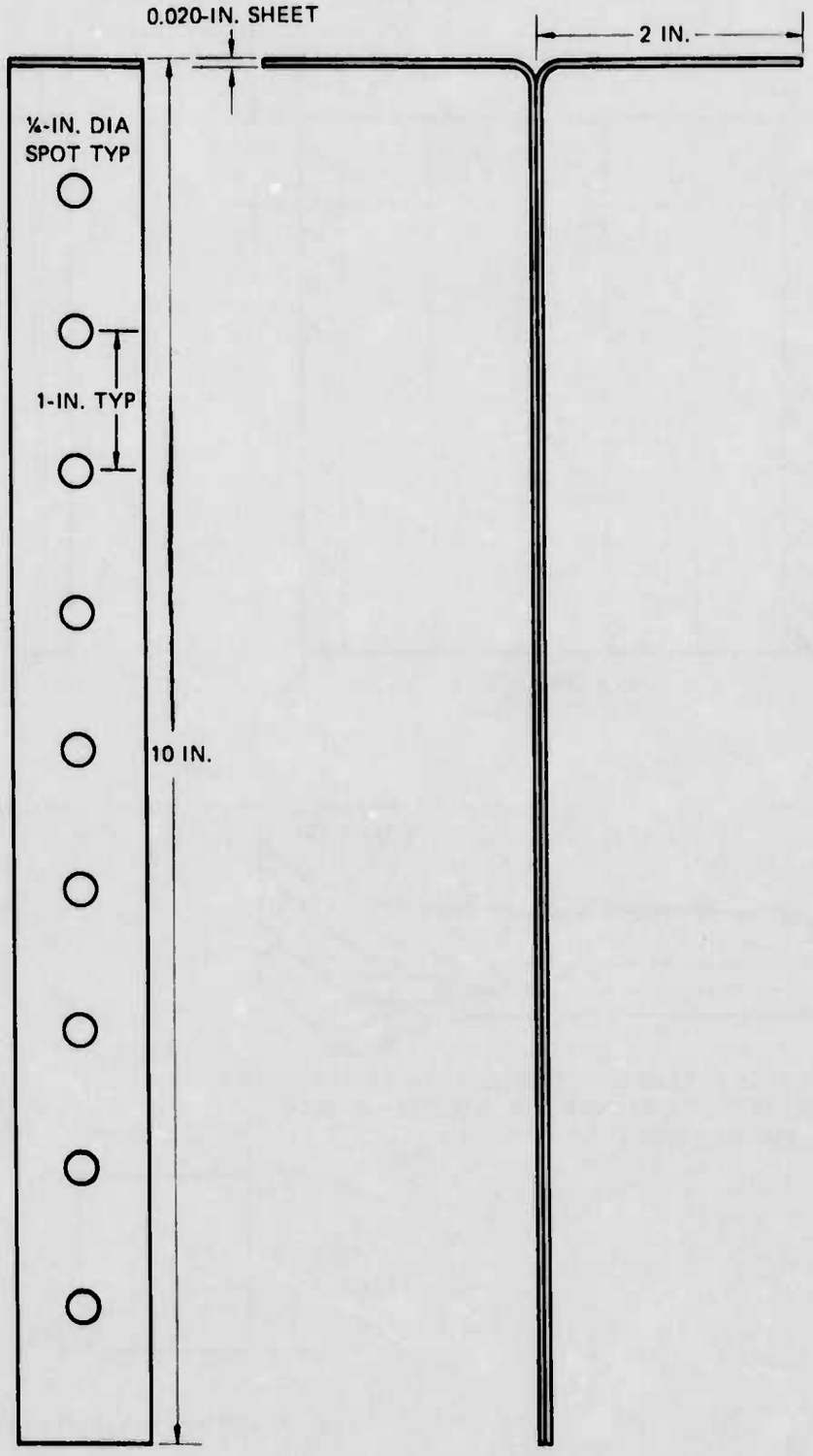


WEDGED CRACK EXTENSION SPECIMEN – THE END AND SIDES OF THE WEDGE SHALL BE APPROXIMATELY FLUSH WITH SPECIMEN END AND SIDES

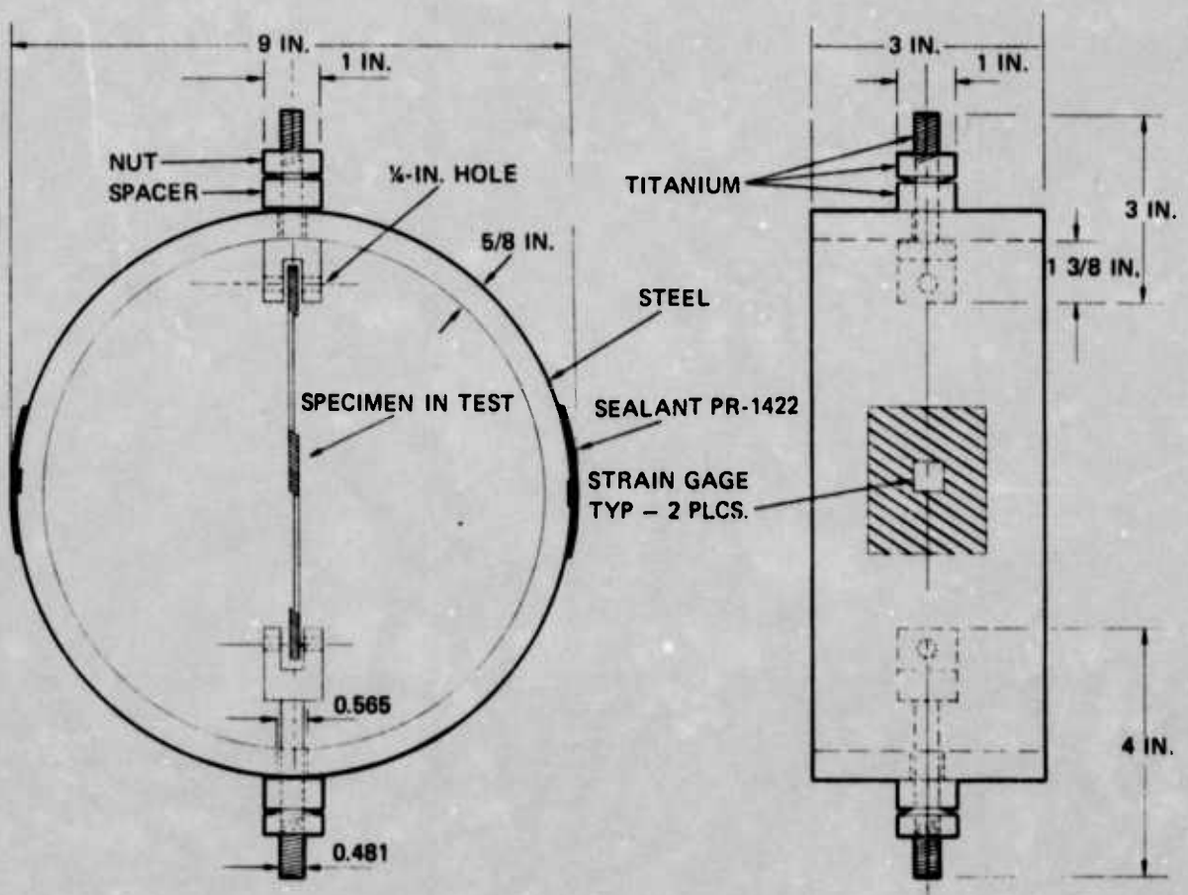


STANDARD WEDGE TEST PANEL AND COUPON

STANDARD "T" PEEL TEST COUPON



STRESS CORROSION FIXTURE WITH STANDARD SHEAR COUPON



NOTE: STEEL PARTS ARE COATED WITH CHEM-MILL MASKANT

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